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PHOTOCHEMISTRY OF THIOPHTHALIMIDES

A THESIS SUBMITTED BY

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A CANDIDATE FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

OF THE

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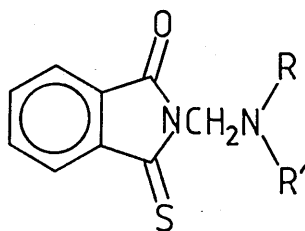
ABSTRACT

Thiomide photochemistry is of interest because previous photochemical studies of thiocarbonyl compounds have been restricted largely to thioketones, and because the "all-oxygen" imides have proved to have a varied and synthetically useful photochemistry. Successful reactions with thiomides might lead to analogous sulphur products that could be readily modified by further chemical reaction.

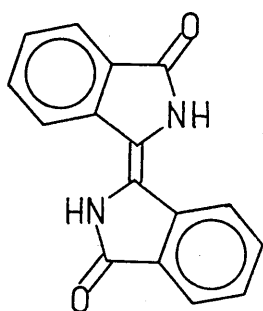
Irradiation of the previously unreported thiophthalimide Mannich bases (A) leads to unusual cleavage products (B and C), unlike the reaction of related phthalimide Mannich bases, which gives photocyclised compounds. Other N-substituted thiophthalimides that might be expected to undergo photocyclisation via hydrogen transfer are unreactive upon irradiation (except to photooxidation).

However, photocycloaddition reactions of N-substituted thiophthalimides with a range of multiply-bonded substrates have proved to be more fruitful. (2+2)-Cycloadducts are obtained with alkenes such as stilbene (adduct structure D), with alkynes such as diphenylethyne (E), with ketenes such as diphenylketene (F), and with ketenimines. These (2+2)-adducts contain thietane or thiete rings, and in some cases ring-cleavage products (G) or ring-opened products (H) are formed. With some alkenes such as methyl acrylate, 2:1 adducts are obtained (I). A substrate (J) designed to produce intramolecular cycloadducts led, surprisingly, to a compound (K) derived by hydrogen abstraction and cyclisation.

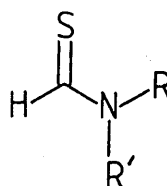
A brief study of the photophysical properties of the N-substituted thiophthalimides shows that they are weakly luminescent at 77 K, and that the reactive excited state is most probably the lowest (n, π^*) triplet.



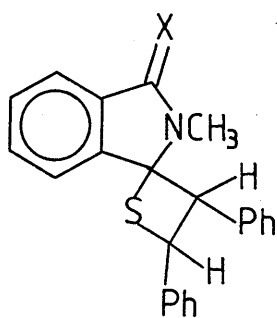
(A)



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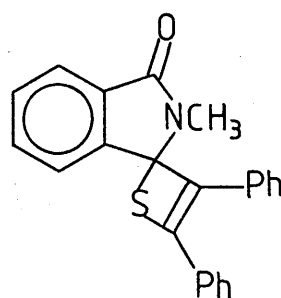


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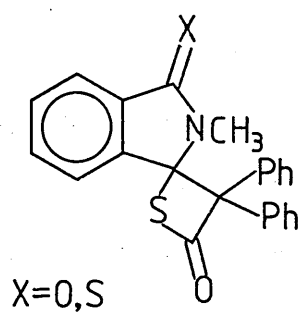


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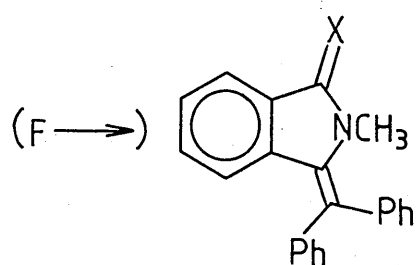
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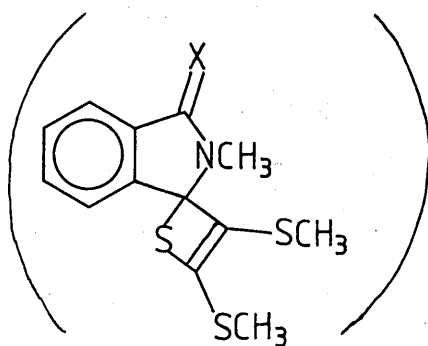
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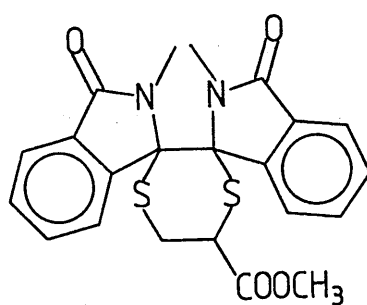
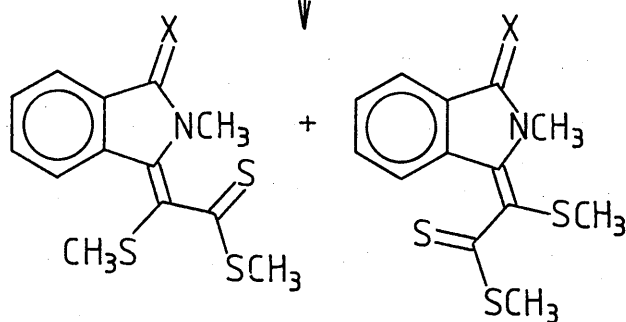
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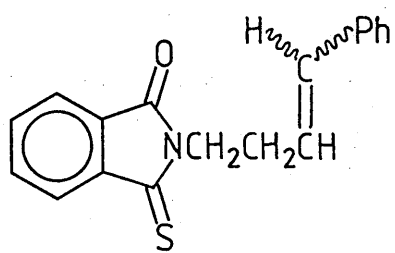
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 $X=O, S$

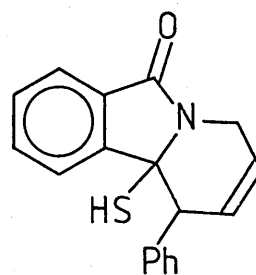
(H)



(I)



(J)



(K)

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2. J.D. Coyle, P.A. Rapley, J. Kamphuis and H.J.T. Bos,
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5. J.D. Coyle and P.A. Rapley, J. Chem. Res., in press.
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J. Chem. Soc., Perkin Trans. I, in press.
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in press.

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CHAPTER ONE

INTRODUCTION

There are two previous areas of research which should be considered in relation to thiophthalimide photochemistry: phthalimide photochemistry and thiocarbonyl photochemistry. These provide reference systems with which the results from thiophthalimides may be compared.

Phthalimide photochemistry

This discussion will include only phthalimide and N-substituted phthalimides. For a more detailed review the reader is referred to Coyle¹ or Mazzocchi².

Excited states

The photochemistry of phthalimides is concerned with four excited states: the first and second excited singlets, which are (n, π^*) and (π, π^*) respectively, and the first and second excited triplets, which are (π, π^*) and (n, π^*) . The proximity in energy of these triplet states and their occasional reversal are interesting features of phthalimide photochemistry, together with detection of fluorescence from the S_2 state.

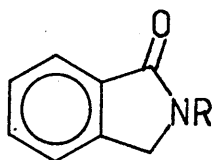
Ground state

The highest occupied molecular orbital in the ground state is the n orbital on a carbonyl oxygen atom. The second highest occupied molecular orbital is a π orbital; results from the photochemistry and values obtained from photoelectron spectral³ measurements and molecular orbital calculations^{3,4} all suggest that the energies of these two orbitals differ only very slightly.

First excited singlet state

The electronic absorption spectra of phthalimides show a strong absorption band around 220 nm, corresponding to a

$S_0 \rightarrow S_3$ electron promotion, a medium intensity band with maxima at 292 and 300 nm, which corresponds to a $\pi \rightarrow \pi^*$ transition (this is the $S_0 \rightarrow S_2$ band), and an extended long wavelength tail at the low-frequency end of the ($\pi \rightarrow \pi^*$) band, which corresponds to $n \rightarrow \pi^*$ electron promotion (this is the $S_0 \rightarrow S_1$ band)⁵. There has been some controversy about whether this latter band is actually attributable to an $n \rightarrow \pi^*$ transition, but the evidence in favour is that this feature does not occur in the spectra of related amides(1)⁵, and it is clearly not due to a charge-transfer band⁵. The $n \rightarrow \pi^*$ transition is expected to be rather weak and possibly hidden by the $\pi \rightarrow \pi^*$ absorption⁶ anyway.



(1)

Decay of the S_1 state occurs non-radiatively: no fluorescence has been observed. The routes by which the S_1 state are depleted are intersystem crossing, non-radiative deactivation to the ground state, and chemical reaction.

First and second excited triplet states

Neither the intersystem-crossing rate constants nor the quantum yields have been measured for phthalimide or N-substituted phthalimides. Decay of the triplet states occurs either non-radiatively, or by phosphorescence, or by chemical reaction. Phosphorescence spectra and lifetimes have been measured for a variety of phthalimides in ethanol glasses at 77 K; typically the lifetimes are ~ 1 second. For phthalimide itself and also for N-(dialkylaminomethyl)phthalimides the first excited triplet state is (π, π^*). That the phosphorescence

is due to a (π, π^*) emitting state is suggested by the long lifetime, the shortening of this lifetime in a brominated solvent, the lack of vibrational fine structure in the spectrum and the out-of-plane polarisation⁵. However for N-propylphthalimide the phosphorescence behaviour suggests that it is possible that the emitting state may be $T(n, \pi^*)$ in this case⁵. The phosphorescence lifetime is only slightly affected by the heavy-atom solvent and the polarisation appears to be mainly in-plane, yet the lifetime is still long and so it is not possible to assign the emitting state with certainty.

Because the energy levels of the (n, π^*) and (π, π^*) triplets are so close it is possible that there may be some mixing of the two, particularly in hydrocarbon solvents which lower the (n, π^*) energy⁵. This is suggested by polarisation measurements on the phosphorescence.

Second excited singlet state

The absorption characteristics have been described above. Fluorescence is weak for the majority of phthalimides ($\phi_f \sim 0.01$), and N-methylphthalimide is reported not to exhibit fluorescence at all⁷. This fluorescence is shown by its excitation spectrum to occur from the $S_2(\pi, \pi^*)$ state⁵. The fluorescence lifetime is ~ 3 ns. Fluorescence from an S_2 state is relatively uncommon, and its observation is an exception to Kasha's rule⁸, which states that emission observed under normal conditions almost always takes place from the lowest excited electronic state for large molecules. The process of internal conversion would be expected to be favoured on Frank-Condon grounds because of the proximity of the energies of the $S_2(\pi, \pi^*)$ and $S_1(n, \pi^*)$ states; however intersystem crossing is in competition with internal conversion.

Self-quenching is demonstrated by the concentration quenching of the fluorescence⁵. Although no mechanism has been proposed for this, it is known not to include an emitting excimer.

Excited state diagram for the N-(dialkylaminomethyl)-phthalimides⁵

395 kJ mol⁻¹ S₂(π,π*) —————

334 kJ mol⁻¹ S₁(n,π*) —————

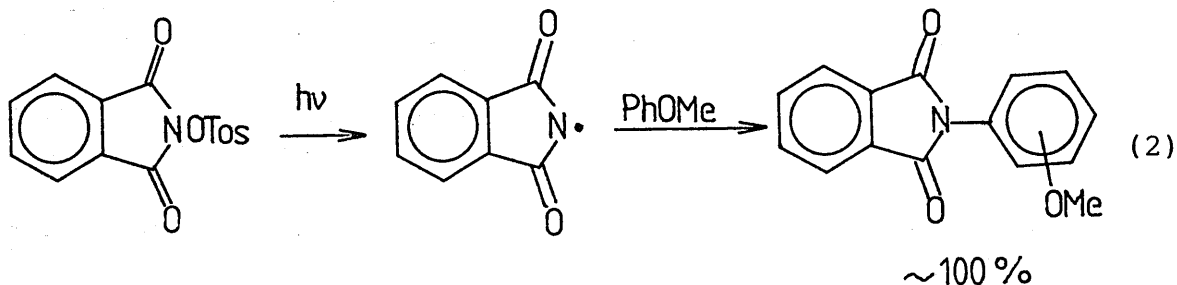
————— T₂ (n,π*) 298 kJ mol⁻¹
 =————— T₁ (π,π*) 288 kJ mol⁻¹

S₀ —————

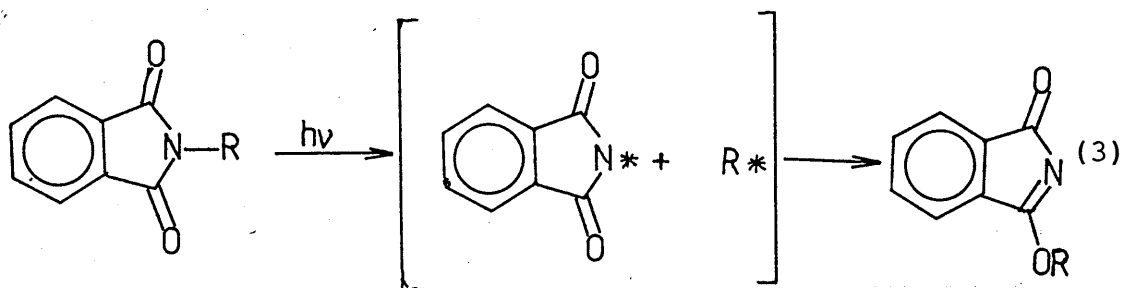
Cleavage reactions

Cleavage alpha to the carbonyl group is not known for phthalimides (although it occurs with aliphatic imides); if α-cleavage does occur, then recombination must be extremely fast with respect to all other processes.

β-Cleavage products are isolated from N-substituted phthalimides in which the N-substituent bond is rather weak, such as N-tosyloxyphthalimide(2)¹². This type of photochemical fragmentation is a good source of phthalimidyl radicals.

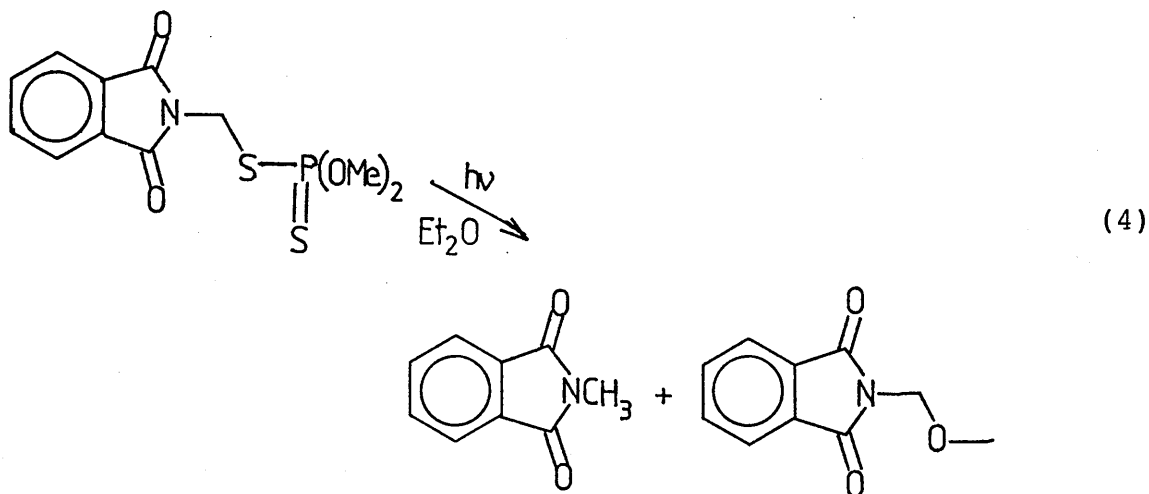


It is possible that β -cleavage is a more general phenomenon among N-substituted phthalimides, but that recombination of the fragments occurs rapidly. The transients observed by Coyle, Harriman and Newport⁹ for N-alkyl- and N-(dialkylaminomethyl) phthalimides were too long lived to be accounted for by excited state species, and it was suggested that these may be attributed to a reaction (3), which could occur from the lowest triplet. The suggested product of this reaction has not been isolated and characterised in the final product mixture from irradiation reactions.



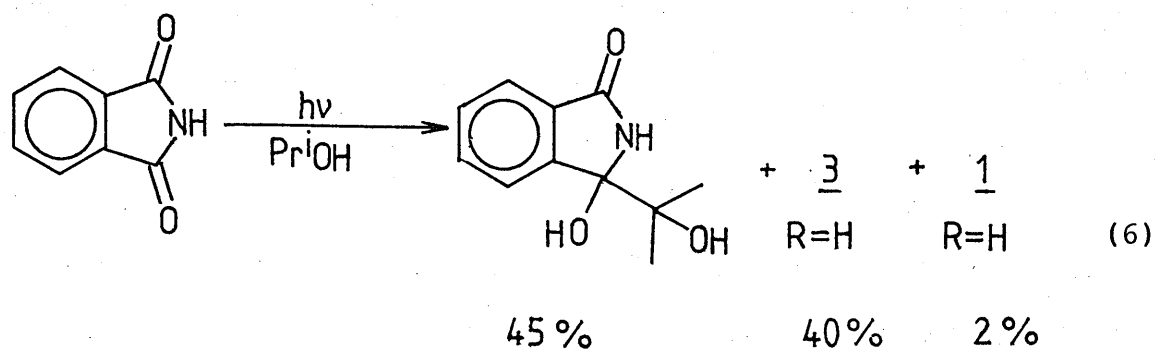
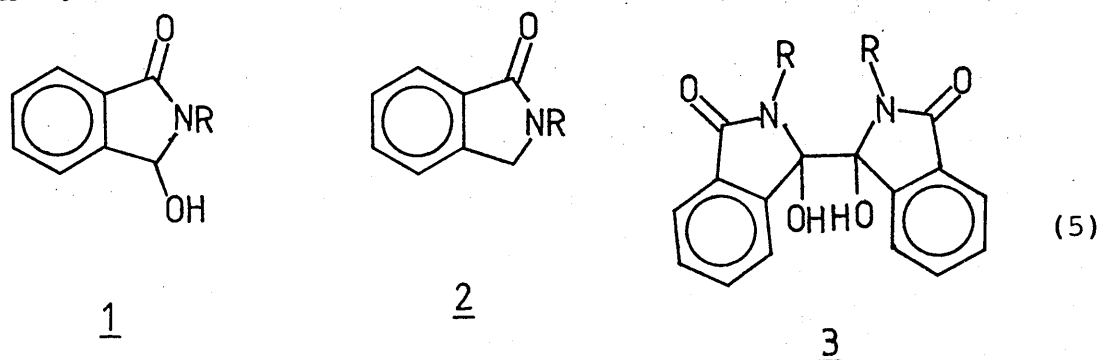
The formation of phthalimides amongst the photoproducts from some N-substituted phthalimides, such as N-(dimethylaminomethyl)phthalimide¹⁰, may arise by β -cleavage.

A γ -cleavage reaction has been observed in the photo-degradation of the insecticide imidan(4)¹¹.



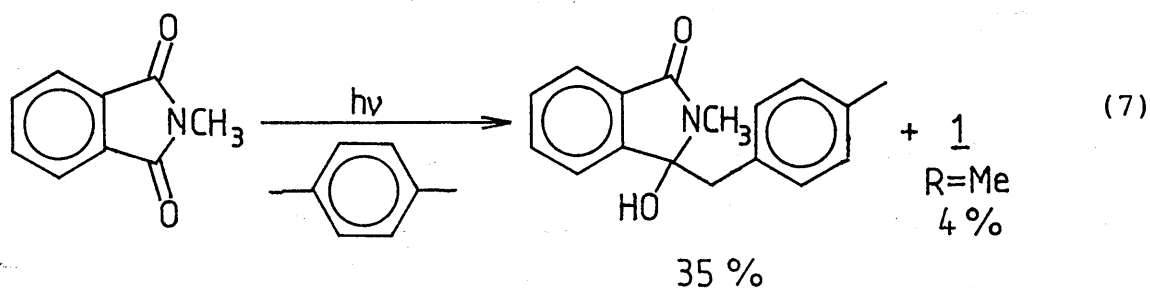
Hydrogen abstraction reactions

These reactions are extensive and will be dealt with in two classes - intermolecular and intramolecular. Intermolecular hydrogen abstraction reactions occur with a wide variety of hydrogen donors^{10,12-19}, including alcohols, ethers, alkenes, amines and alkylbenzenes. The photoreduced products are of the three types shown (5). Photoaddition products are also possible and mixtures are often formed. With phthalimide and propan-2-ol the major products are the photoadduct and the dimer (6)¹⁶. Similar photoreactions are observed for phthalimide in the presence of ethanol, dioxan or tetrahydrofuran¹⁶.

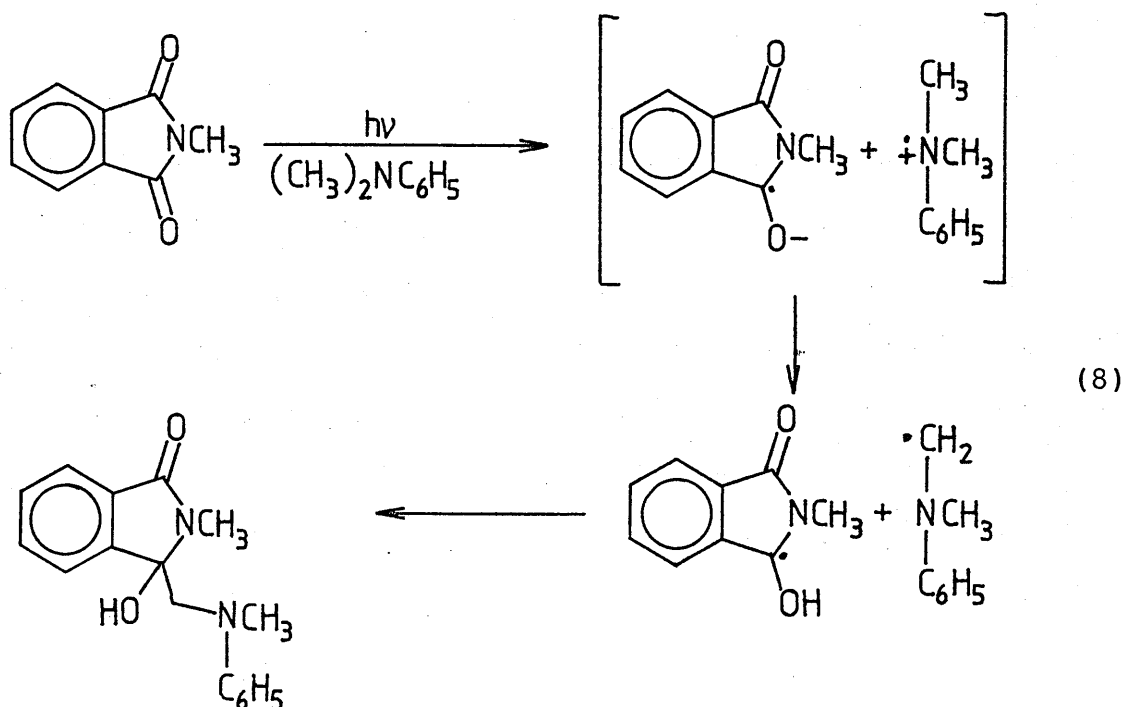


N-Methylphthalimide has been the subject of studies using a wide variety of hydrogen donors. In the presence of an alcohol it gives 3-hydroxy-2-methylisoindolin-1-one (1, R = Me) together with the photoaddition product¹³ in a reaction parallel to that of phthalimide. Photoreduction of N-methylphthalimide by ethers such as dioxan, diethyl ether or tetra-

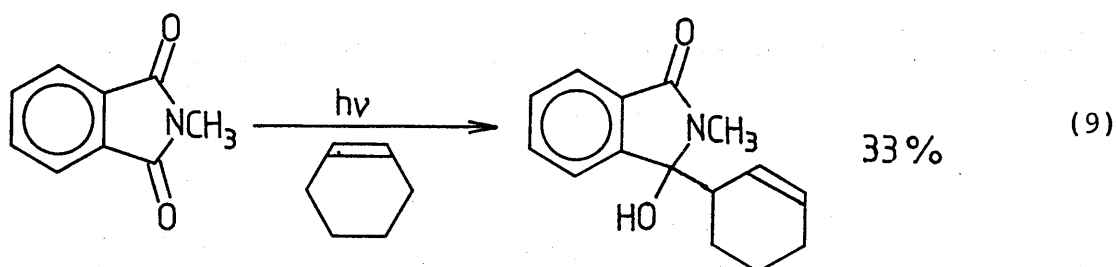
hydrofuran^{19,20} also leads to 3-hydroxy-2-methylisoindolin-1-one (1, R = Me) together with the diastereomeric addition products. The hydrogen atom which is abstracted in each case is adjacent to a heteroatom, which must therefore stabilise the intermediate. The same conclusion may be drawn for hydrogen abstraction from alkylbenzenes^{18,21}, which lead to both addition and photoreduction products (7).



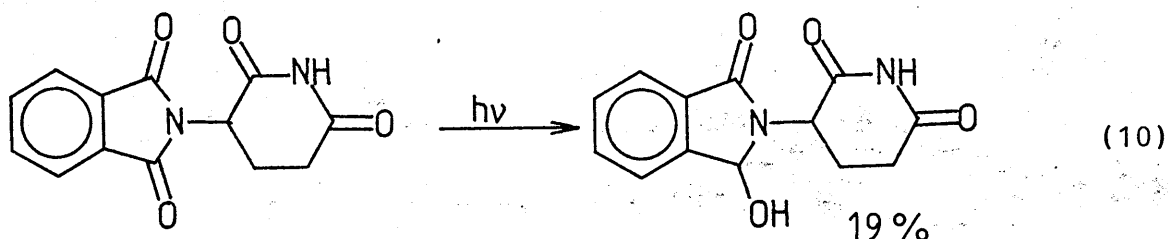
Kanaoka²² implies that direct hydrogen abstraction may take place in some cases, although there is as yet no mechanistic evidence to support this. It is suggested that the photoreduction reaction of the phthalimides occurs by initial electron transfer followed by proton transfer and radical coupling (8)¹⁸.



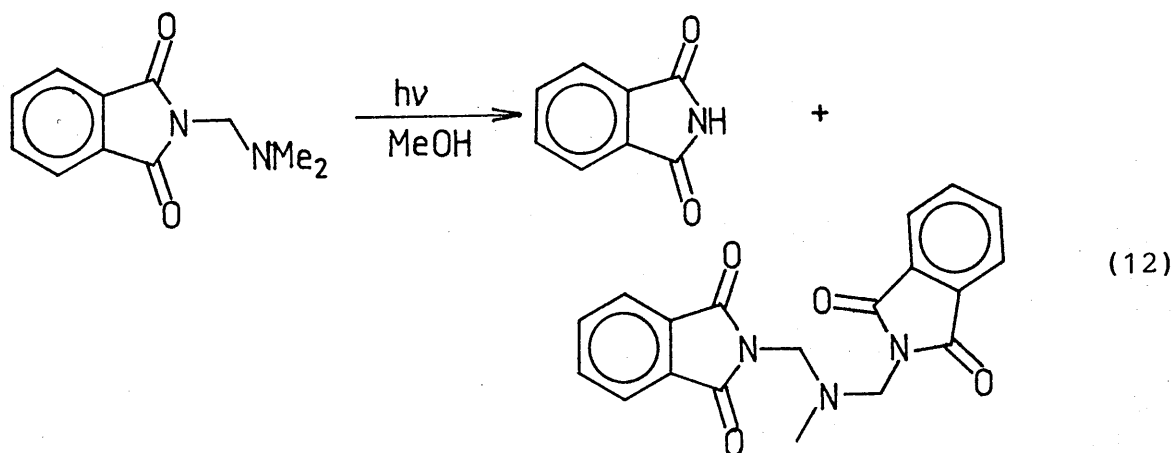
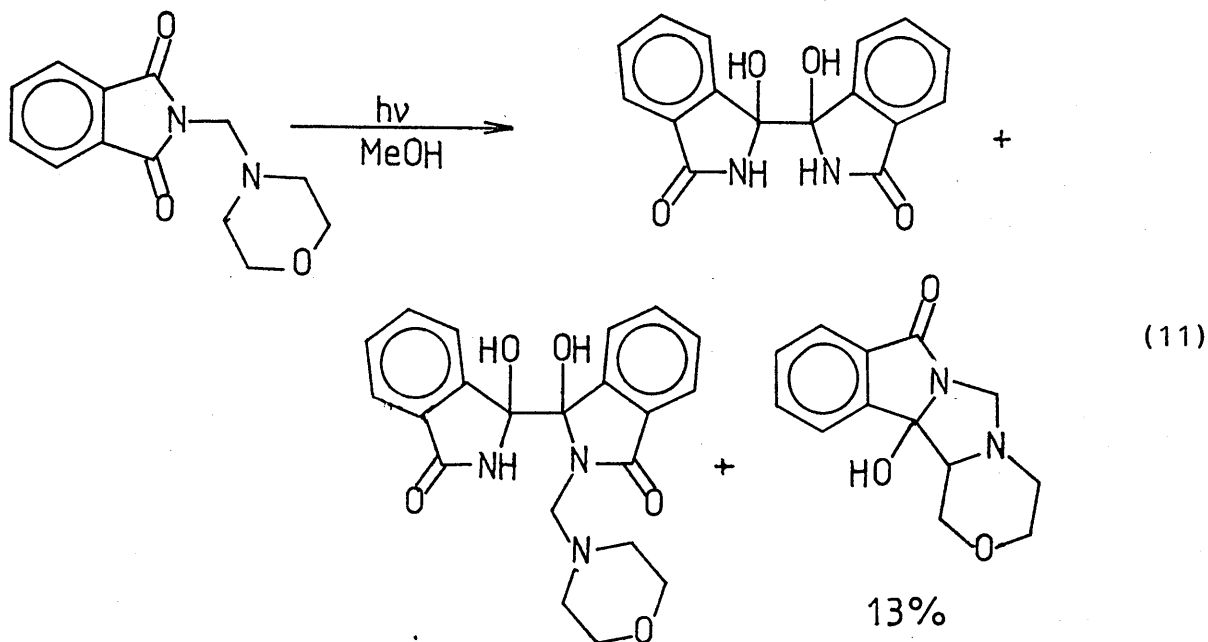
Reaction of N-methylphthalimide with triethylamine leads to the relatively unusual N-methylphthalimidine (2, R = Me) as a product¹⁸. Photoaddition products are observed following the abstraction of an allylic hydrogen from an alkene such as cyclohexene or cyclopentene(9)¹⁹. However the overall yield of this reaction is not particularly high and there are competing photocycloaddition reactions (to be discussed later) with some alkenes.



The photoreduction of some more elaborately substituted phthalimides has also been studied. N-(Methoxymethyl)phthalimide and N-(carboxymethyl)phthalimide give photoaddition products on irradiation with tetrahydrofuran¹⁶, but irradiation of thalidomide under similar conditions leads only to the reduced (hydroxyisoindolone) product(10)¹².



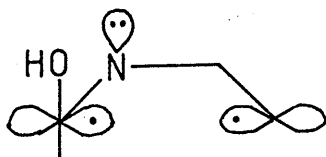
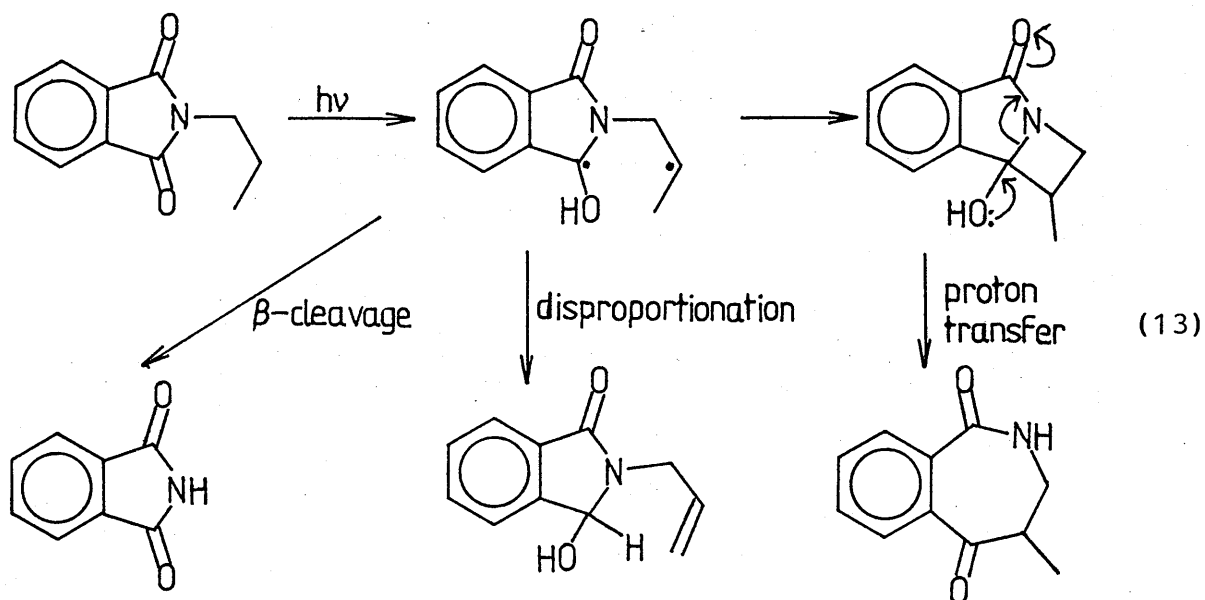
Photoreduction has also been observed as a side reaction in the photochemistry of N-(morpholinomethyl)phthalimide¹⁷ (the main reaction is an intramolecular hydrogen abstraction (11)). It appears that fragmentation to phthalimide is also occurring, as was the case for N-(dimethylaminomethyl)-phthalimide(12)¹⁰.

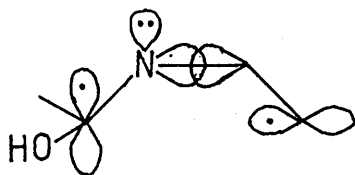


Intramolecular hydrogen abstraction reactions are similar to the intermolecular ones, and are of synthetic utility in that they provide a good route to a variety of heterocyclic systems including some interesting macrocycles.

The simplest systems of this type which have been studied are the N-alkylphthalimides²³. In alcohol solvents, only benzazepinediones, resulting from initial γ -hydrogen abstraction, are observed as the major products on irradiation, but in acetone or acetonitrile minor amounts of phthalimide and the N-allylic-3-hydroxyisoindolinone are formed(13). The reaction

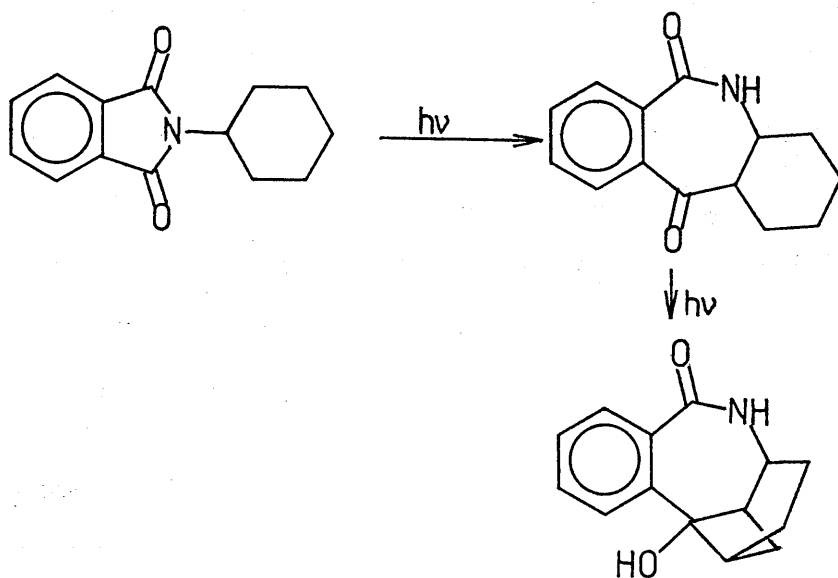
which has been shown here for N-propylphthalimide is fairly general; exceptions are N-t-butylphthalimide, which gives phthalimide as a significant product, and N-(3-methylbutyl)-phthalimide, which shows hydrogen abstraction from a position other than the γ -position. The comparatively favourable formation of the intermediate fused azetidinol (and hence the benzazepinedione) can be rationalised by considerations of orbital overlap in the biradical. Cleavage of the C-N bond would require overlap of the C-N σ -orbital with both of the orbitals containing single electrons, as in (14); however the orbital at the carbon carrying the OH group is stabilised by overlap with the lone-pair orbital of nitrogen, as in (15), and thus β -cleavage does not occur readily.





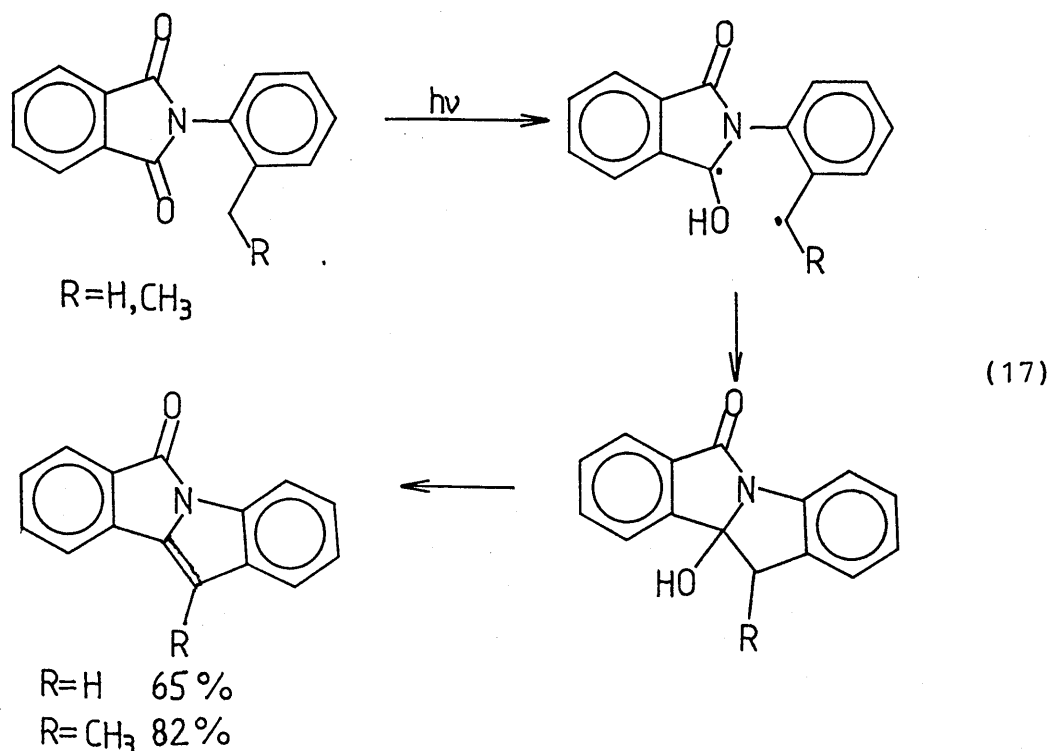
(15)

Mechanistic studies of benzazepinedione formation showed a selectivity difference for tertiary γ -hydrogen abstraction over primary γ -hydrogen abstraction of about ten to one. The quantum yields for product formation are rather low ($\sim 8 \times 10^{-3}$); it has been shown that this is not due to the reversible formation of a long-lived biradical, because optically active N-(2-methylbutyl)phthalimide does not racemise under the reaction conditions²⁴. It seems likely that the reaction occurs via the (n, π^*) singlet state; both quenching studies²⁵ and phosphorescence measurements on a variety of N-substituted phthalimides⁵ would support this. The reaction has been extended to include N-cyclopentyl and N-cyclohexylphthalimide²⁵: from the former the product is a benzazepinedione, but from the latter the product is an interesting polycyclic system which arises from a further photochemical reaction of the benzazepinedione (16).



(16)

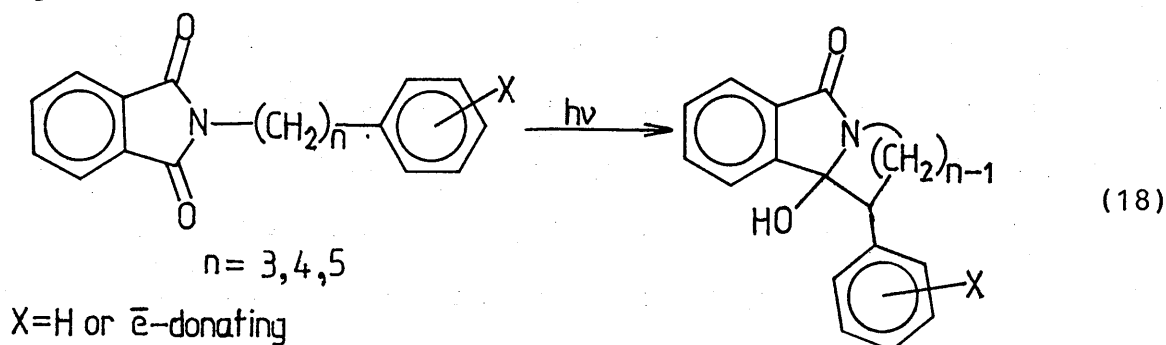
A variety of systems in which hydrogen abstraction occurs at a position other than the γ -position have also been investigated. One such type of reaction which has received considerable attention is that undergone by the N-(o-alkylaryl) phthalimides¹³, in which the fused-ring system which is formed readily dehydrates to produce an indole derivative(17).



Kanaoka et al. suggested that these efficient reactions occur via a seven-membered cyclic transition state and that free-radical intermediates were involved. The electronic effects operating in the excited state have been investigated on a series of N-o-tolylphthalimides with different substituents on the phthalimide ring and on the other aromatic ring²⁶. It was found that electron-donating groups on the N-o-tolyl ring increased the yield of products formed in a specific time, whereas electron-withdrawing groups decreased it. However, on the phthalimide ring electron-withdrawing groups led to a higher yield of products formed in a specific time, whereas electron-donating groups (e.g. $-NH_2$, $-OMe$) led to lower yields. These effects are explained as being due to

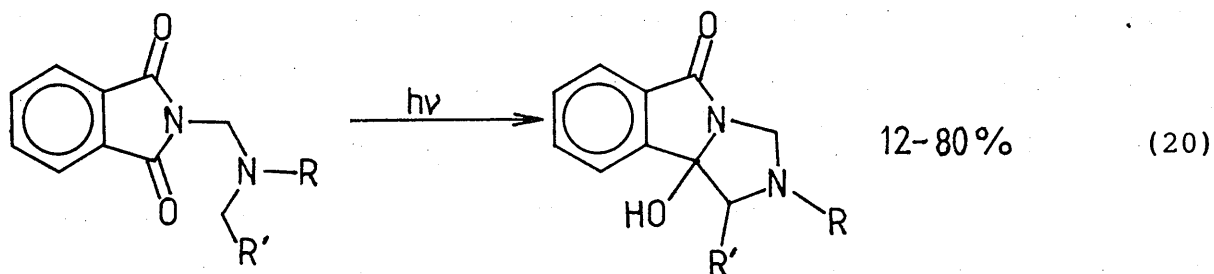
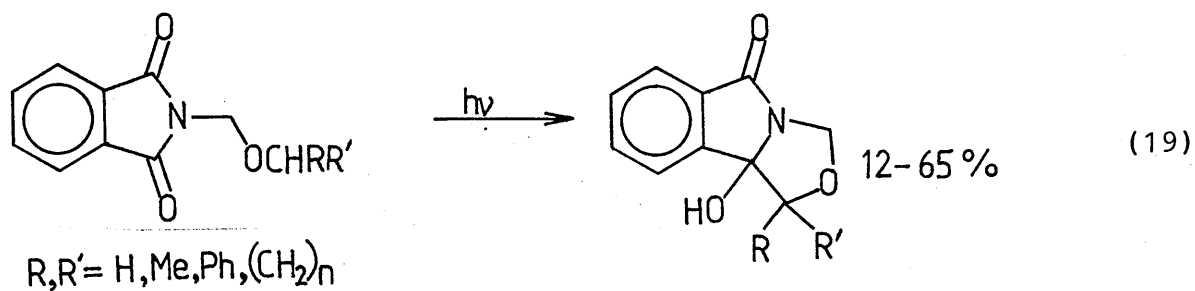
stabilisation of an incipient radical by the N-o-tolyl ring, whereas the change in reactivity associated with substituents on the phthalimide ring may result from an inversion of the (n,π^*) and (π,π^*) triplet states. The (π,π^*) triplet might be expected to be less reactive by comparison with ketones.

In a homologous series of N-(ω -arylalkyl)phthalimides²⁷ hydrogen abstraction takes place adjacent to the aromatic ring(18).

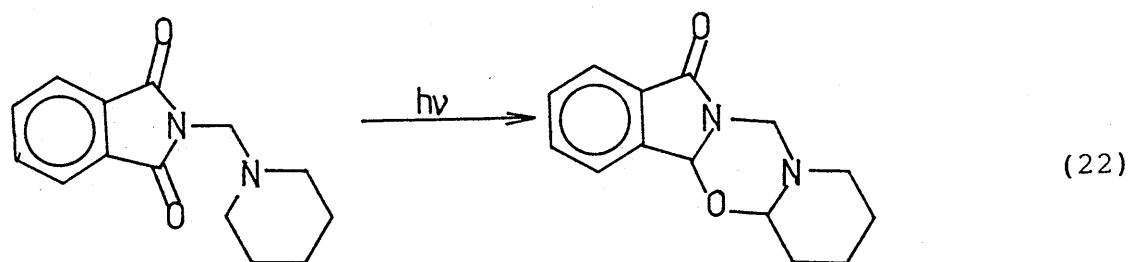
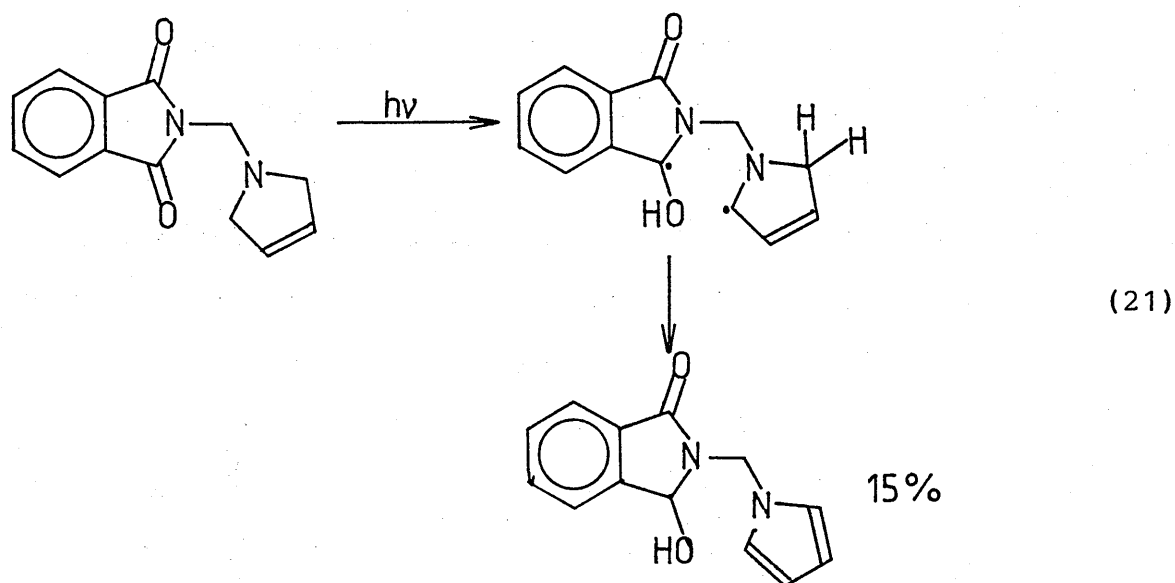


The highest yields were obtained for $n = 4$, and the authors suggested that the reaction occurs via an eight-membered cyclic transition state. It is likely that there is a charge-transfer interaction in the ground state between the electron-deficient phthalimide ring and the electron-rich aromatic ring; this proposal is supported by fluorescence results, both of the substrates and of related systems^{22(b), 28}.

If there is a heteroatom present in the side chain then this affects the preferred position of hydrogen abstraction. A heteroatom at the γ -position leads to the major product by way of hydrogen abstraction at the δ -position. This appears to be the case for oxygen, sulphur or nitrogen, as shown by the reactions of N-(alkoxymethyl)phthalimides^{29, 30} (19), N-(alkylthiomethyl)phthalimides³¹, and N-(dialkylaminomethyl)phthalimides^{14, 15, 32, 33} (20).

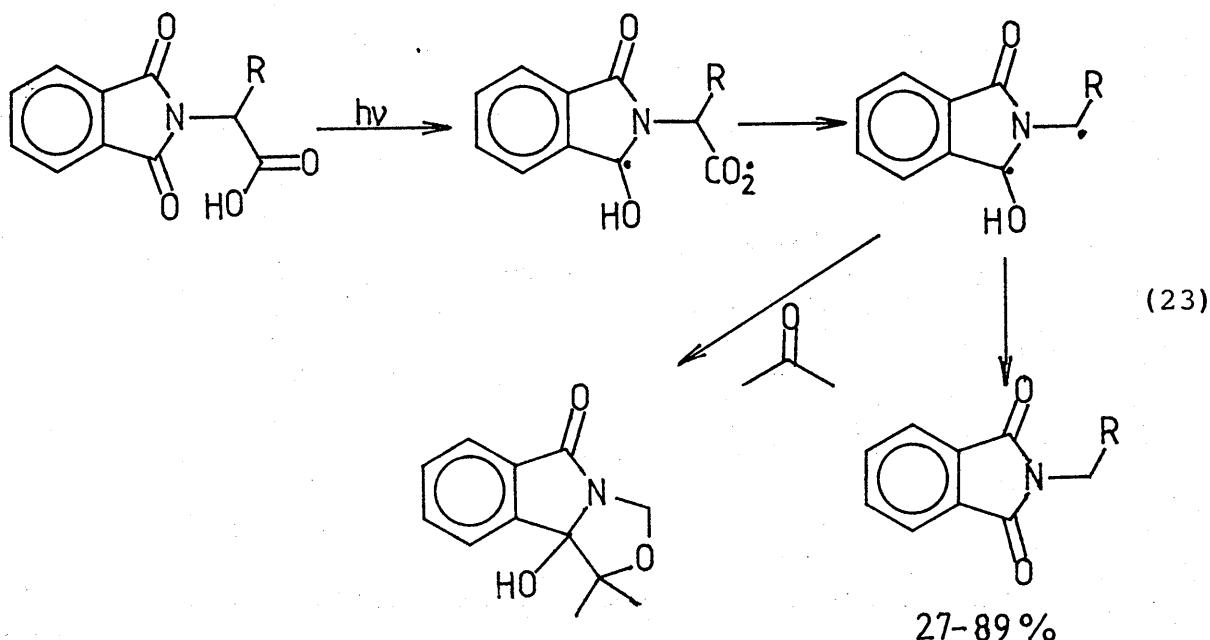


Reactions which compete with the cyclisation may give rise to alternative products, for example N-(3-pyrrolin-1-ylmethyl)phthalimide gives a substituted hydroxyisoindoline upon irradiation(21)³³, and the irradiation of N-(piperidino-methyl)phthalimide¹⁵ gives an oxadiazine(22).

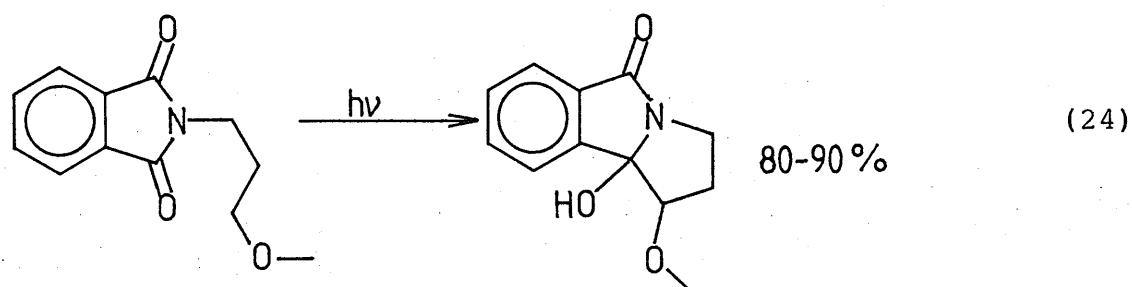


The mechanism of the reactions of N-(dialkylaminomethyl)-phthalimides has been investigated⁵, and the results suggest that the photochemical reactions involve electron transfer as the primary step.

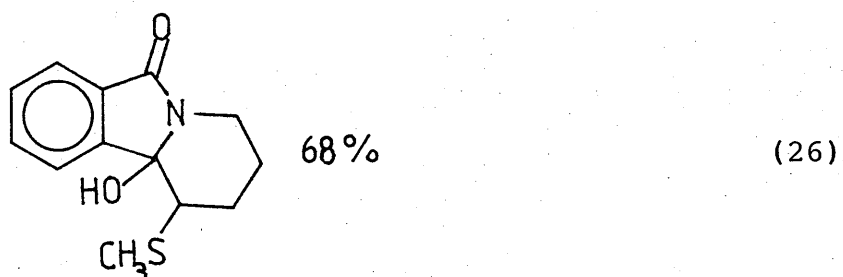
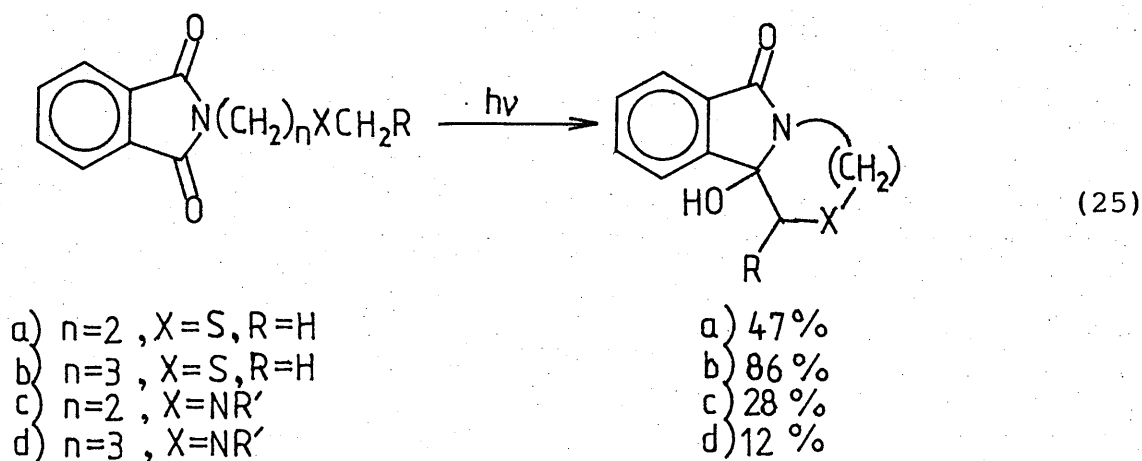
With N-phthaloyl α -aminoacids, abstraction of the acidic hydrogen takes place to yield a biradical that may decarboxylate²⁰; the decarboxylated biradical can undergo internal disproportionation, or it may be trapped by added acetone.



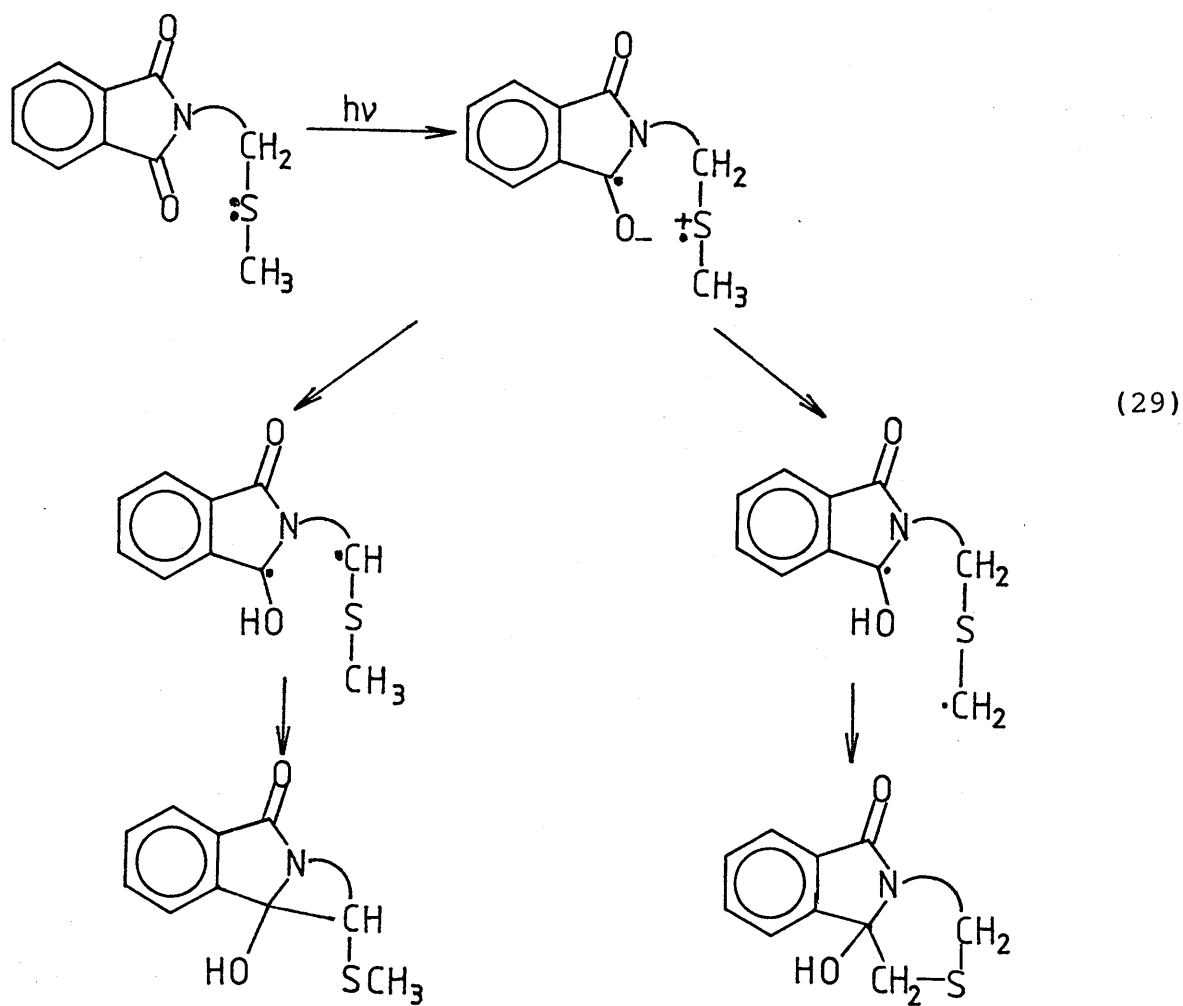
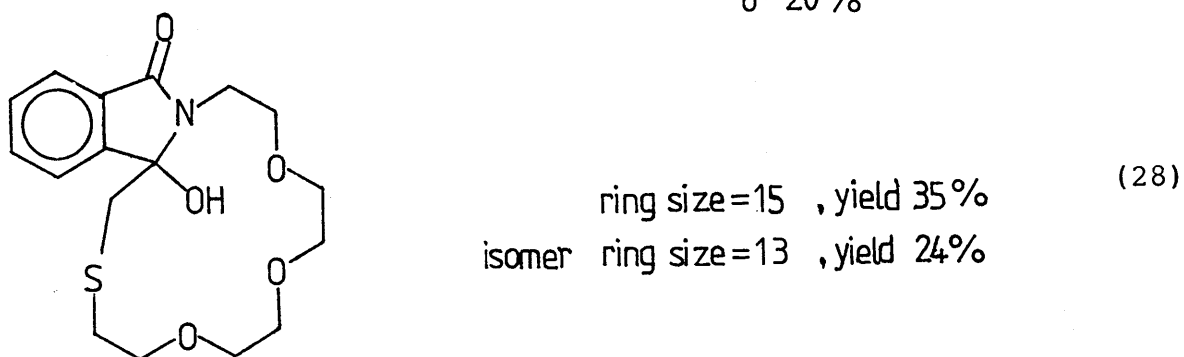
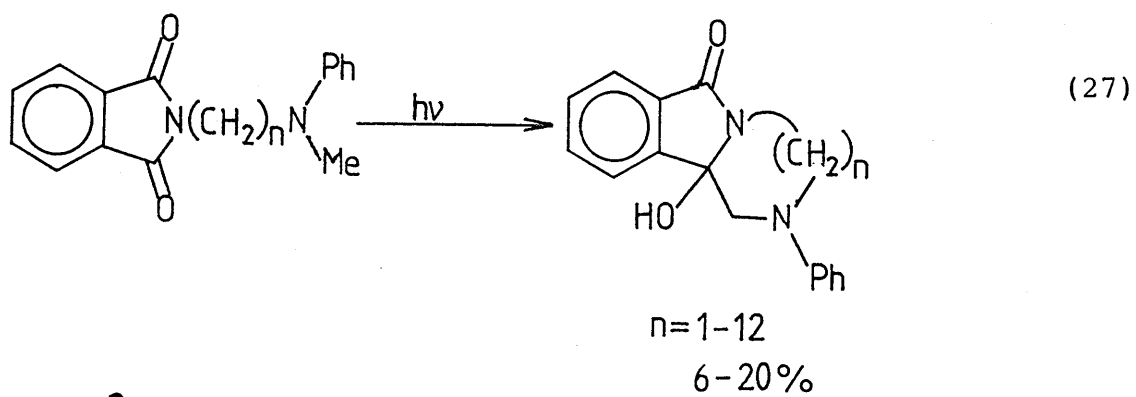
Other systems of interest have been N-substituted imides in which the alkyl side-chain contains a heteroatom at a position other than the γ -position. Such compounds allow a choice of abstraction positions, and herein lies their fascination. If there is an oxygen atom in the ϵ -position, then there is a preference for δ -hydrogen abstraction²⁹. The authors suggest that the driving force for δ -hydrogen abstraction via a seven-membered cyclic transition state may be due to favourable geometric factors.



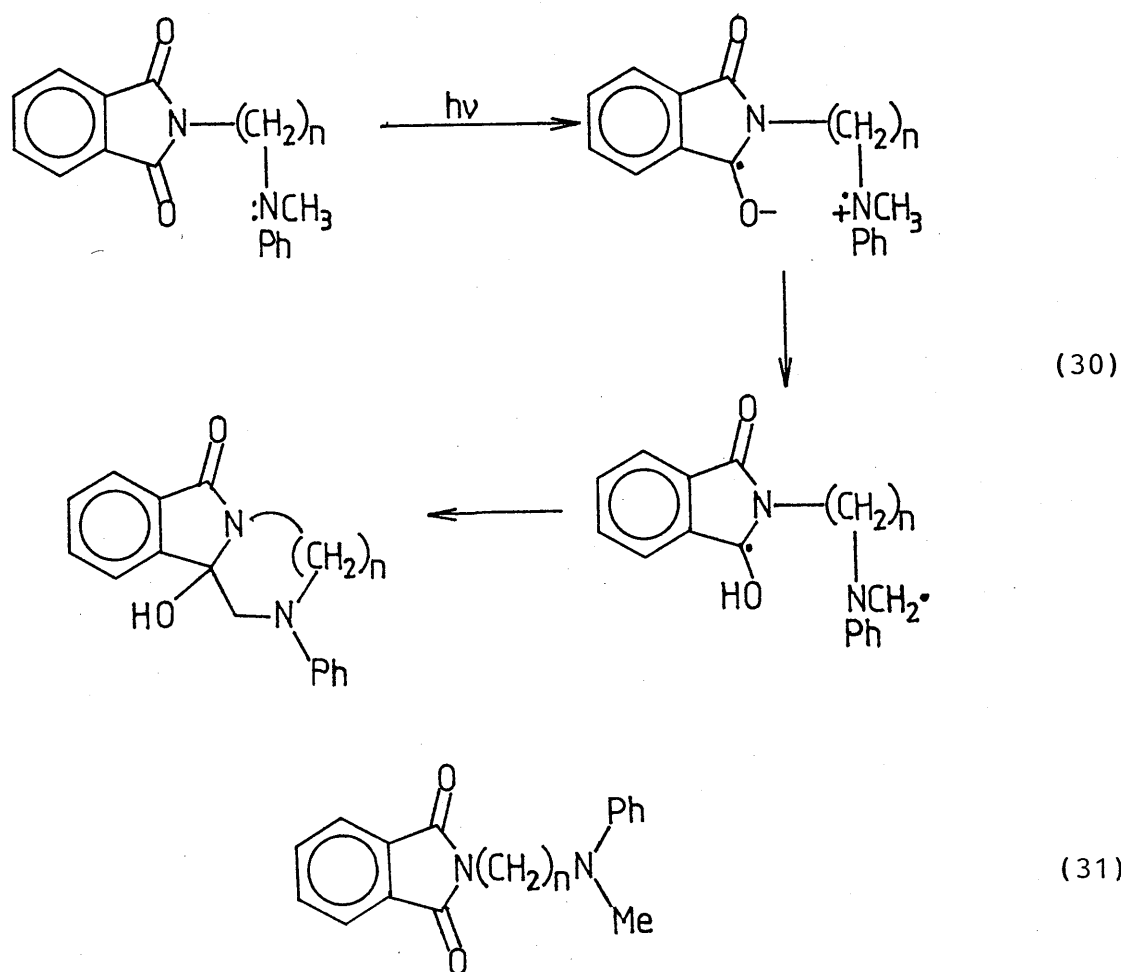
With nitrogen or sulphur in the side-chain the heteroatom is generally endocyclic in the product (25),^{31,34,35}, although for $n = 4$, $X = S$, $R = H$ a product with an exocyclic heteroatom is observed (26)³¹.



The reactions with nitrogen or sulphur substituents can be extended to give larger ring systems (27)^{36,37} and for sulphur it is possible to form some spectacular macrocycles (28)^{38,39}. The success of these macrocyclic syntheses suggests that a charge-transfer mechanism is operating, in which there is electron transfer followed by proton transfer (29). Evidence supporting this is the existence of a weak charge-transfer band between N-methylphthalimide and 1-(methylthio)butane³⁷.



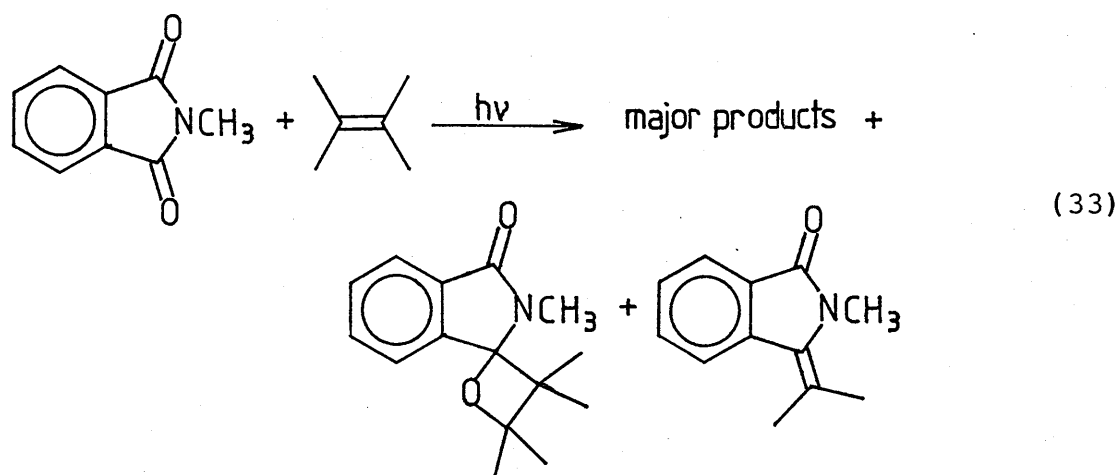
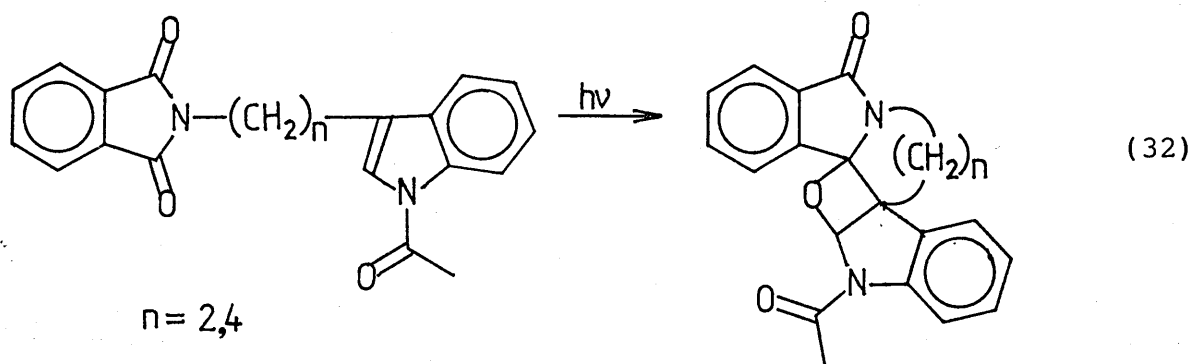
Kanaoka has suggested that the medium and large ring nitrogen compounds are formed from a radical-anion radical-cation pair which is generated after an initial electron transfer (30)³⁶. Evidence for such electron transfer arises from other work, by Coyle, Newport and Harriman⁵, who observed a charge-transfer absorption band for the *N*-(dialkylaminomethyl) phthalimide (31, $n = 1$), and by the Davidson group⁴⁰, who reported that *N*-substituted phthalimides (31, $n = 0 - 4$) showed charge-transfer absorption bands and fluorescence (no fluorescence for $n = 0$, however). These results suggest that the systems react via the singlet state.



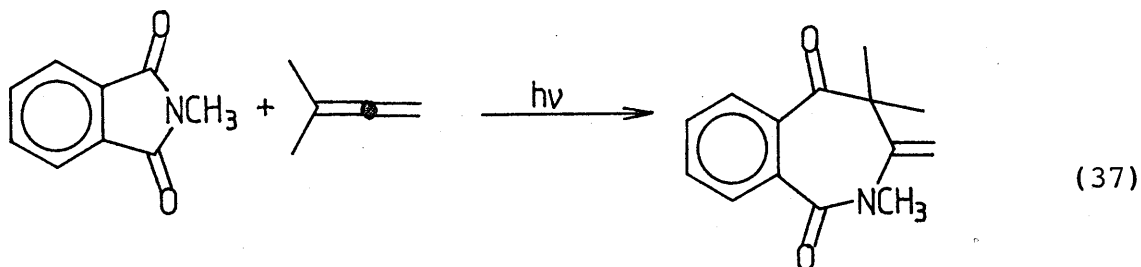
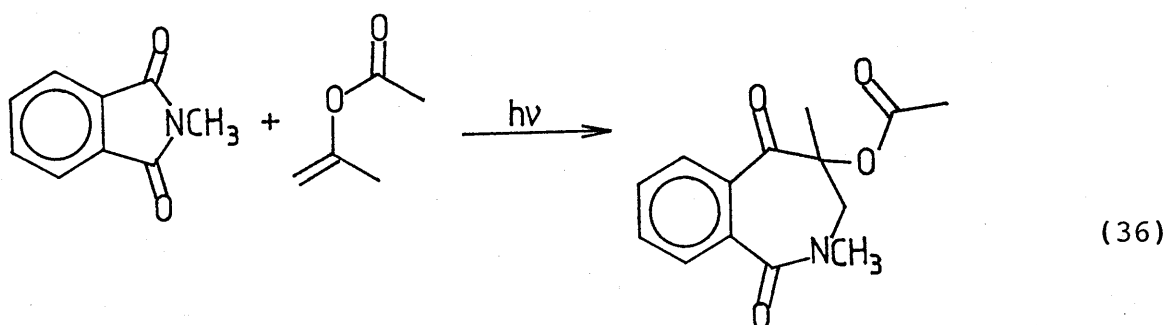
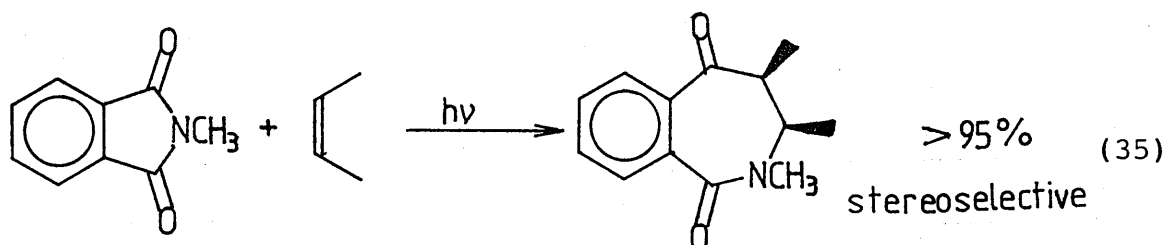
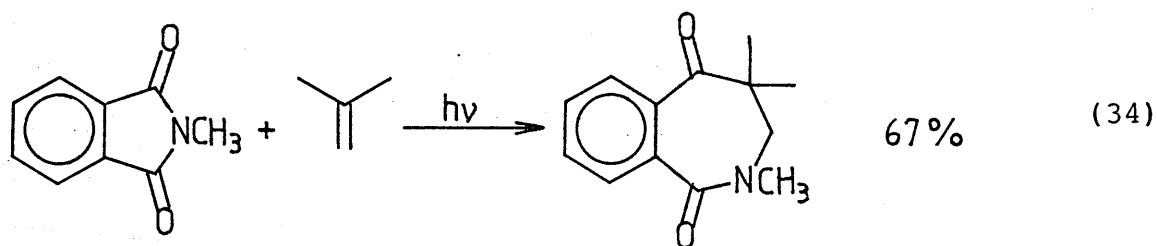
Photocycloaddition reactions

Irradiation of phthalimides with alkenes does not generally lead to the oxetane products which might be expected by comparison with ketones or alicyclic imides². Recently oxetane

products have been isolated following the irradiation of N-(ω -indol-3-ylalkyl)phthalimides(32)⁴¹, and also as a minor product in the irradiation of N-methylphthalimide with 2,3-dimethylbut-2-ene(33) or styrene⁴². With 2,3-dimethylbut-2-ene oxetane formation was shown, by quenching and sensitisation studies, to arise via the triplet state⁴³. However, such oxetane products are the exception rather than the rule.

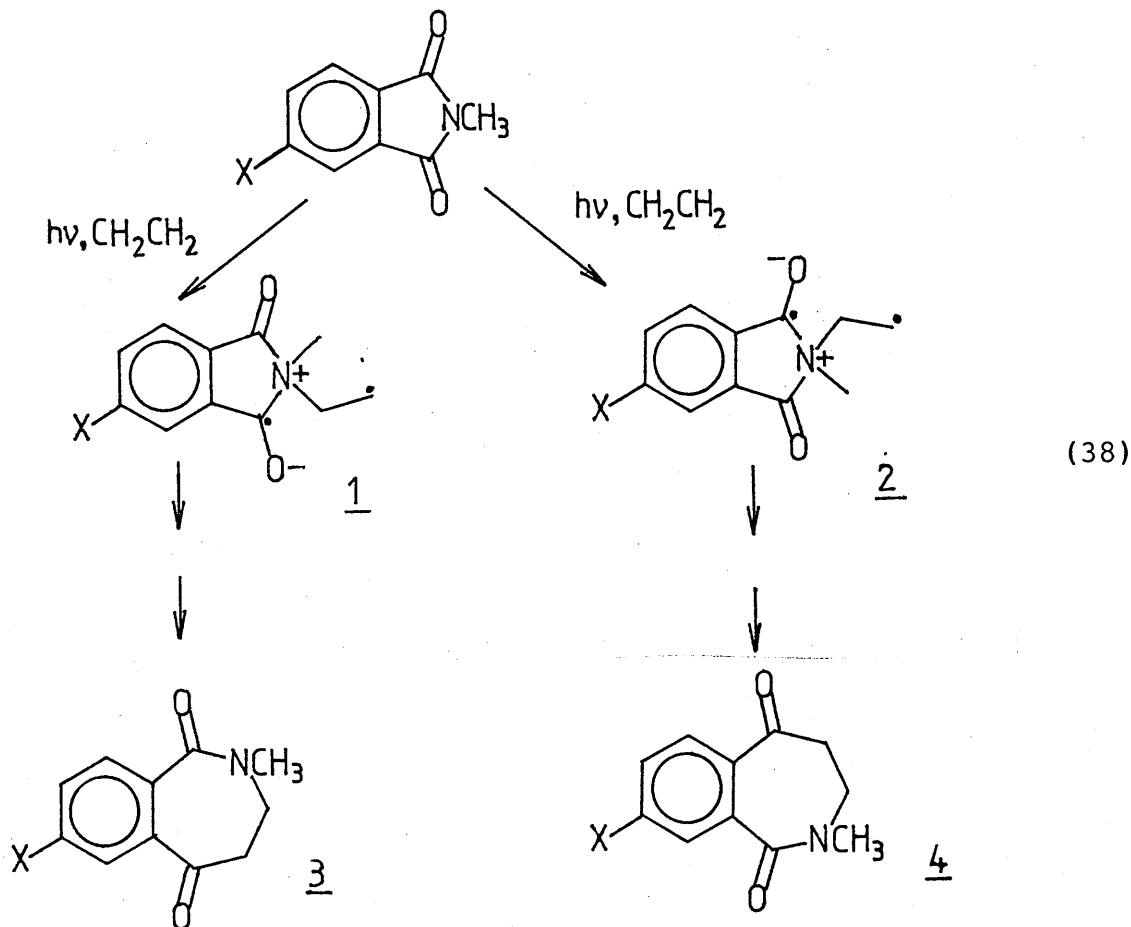


The reaction of phthalimides with alkenes gives mainly benzazepinediones, and the process is regiospecific(34)⁴⁴ and highly stereoselective(35)⁴⁵. The reaction has some generality in that it also occurs for certain conjugated dienes, alkenes, vinyl ethers, vinyl esters(36) and an allene (37). The reaction is not successful for electron - deficient alkenes such as ethyl acrylate or acrylonitrile^{2,46}.



The mechanism of the reaction has been studied extensively by the Mazzocchi group. It seems that benzazepinedione formation is a singlet state process⁴⁷, presumably occurring from the (n, π^*) singlet. Two mechanisms can be considered²: a biradical mechanism and a concerted mechanism. The biradical mechanism appears to explain the regiospecificity, but if this were the case then cis-but-2-ene and trans-but-2-ene would be expected to give the same product mixture unless ring-closure occurred at a rate faster than rotation around the C-C bond.

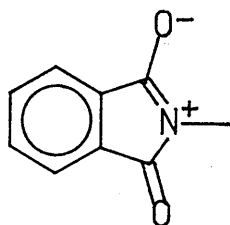
However, experiments in which crude reaction mixtures are examined at low conversion indicate that the process is completely stereospecific⁴⁵. The other evidence against the biradical mechanism arises from work on the directive effect of substituents on the phthalimide ring⁴⁸.



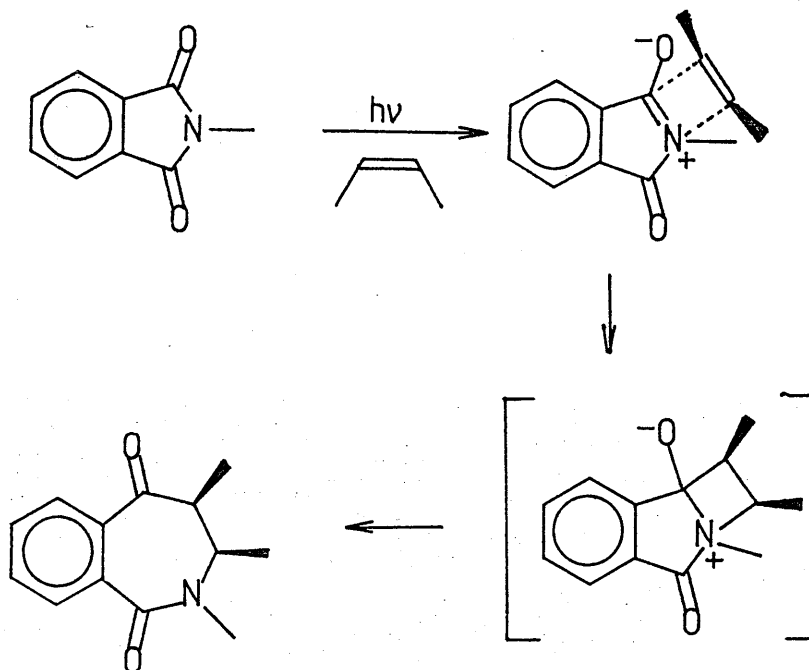
The stabilities of the radical ions 1 and 2 are dependent on the electron-withdrawing or electron-donating nature of the substituent X; however, the products are found to be opposite from those which would be predicted in this way, and so the biradical mechanism appears to be unlikely.

All available evidence points to a concerted [2+2] addition which takes place via an exciplex. The resonance canonical (39)⁴⁶ would be expected to contribute substantially to the excited state structure, and the formation and collapse of an exciplex would explain the stereospecificity of the

benzazepinedione formation (40)⁴⁸. The regiochemistry is proposed by the authors⁴⁶ as being due to HOMO-LUMO interactions.

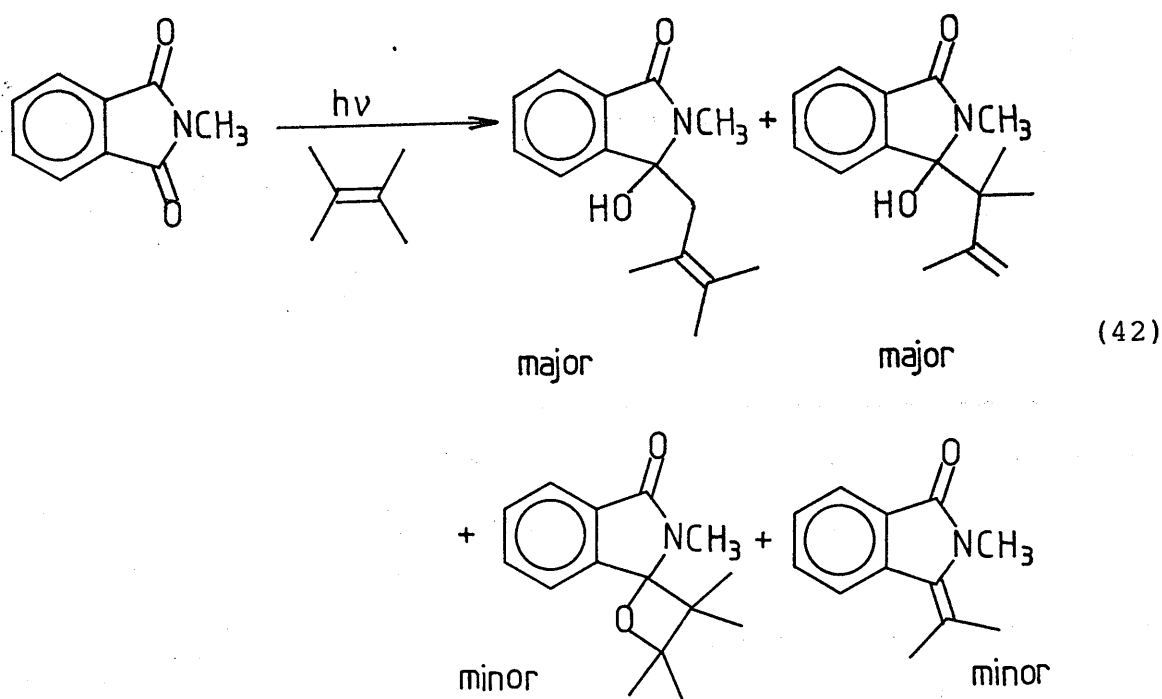
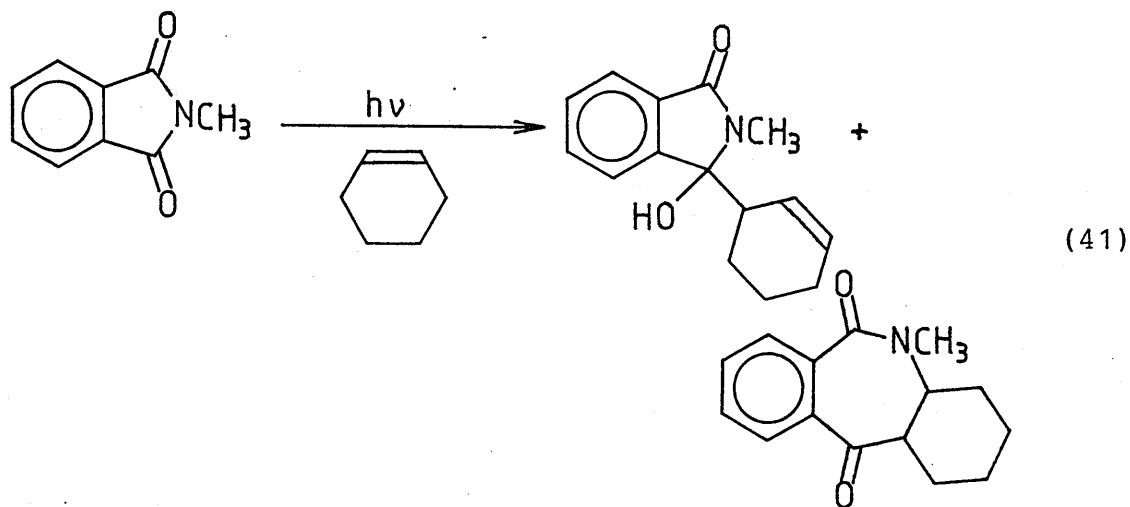


(39)



(40)

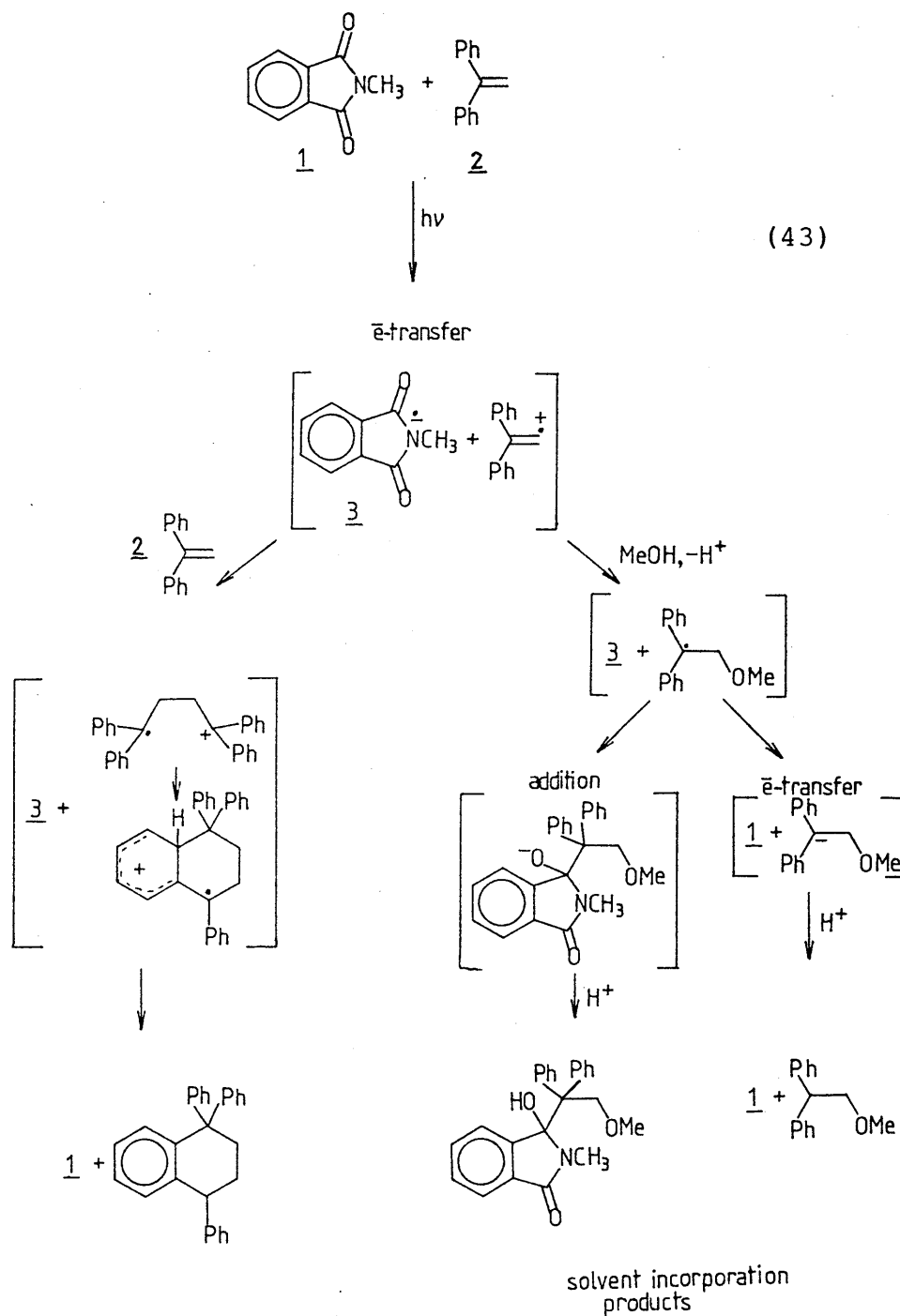
One feature of the reaction to form the benzazepinediones is the fact that it will not go for all alkenes, and alkene reactivity can be correlated to ionization potential^{46,49}. Alkenes having a low ionization potential, such as 2,3-dimethylbut-2-ene, do not react to give benzazepinedione products, whereas alkenes with a higher ionization potential, such as but-2-ene, give benzazepinedione products. This result has been interpreted to mean that there is a competing electron-transfer reaction, and indeed the formation of a radical anion-radical cation pair has been demonstrated by trapping experiments.⁵⁰ Thus photoreduction may be in competition with cycloaddition for some alkenes such as cyclohexene (41)¹⁹, or may supercede it, as for 2,3-dimethylbut-2-ene (42)⁴³.

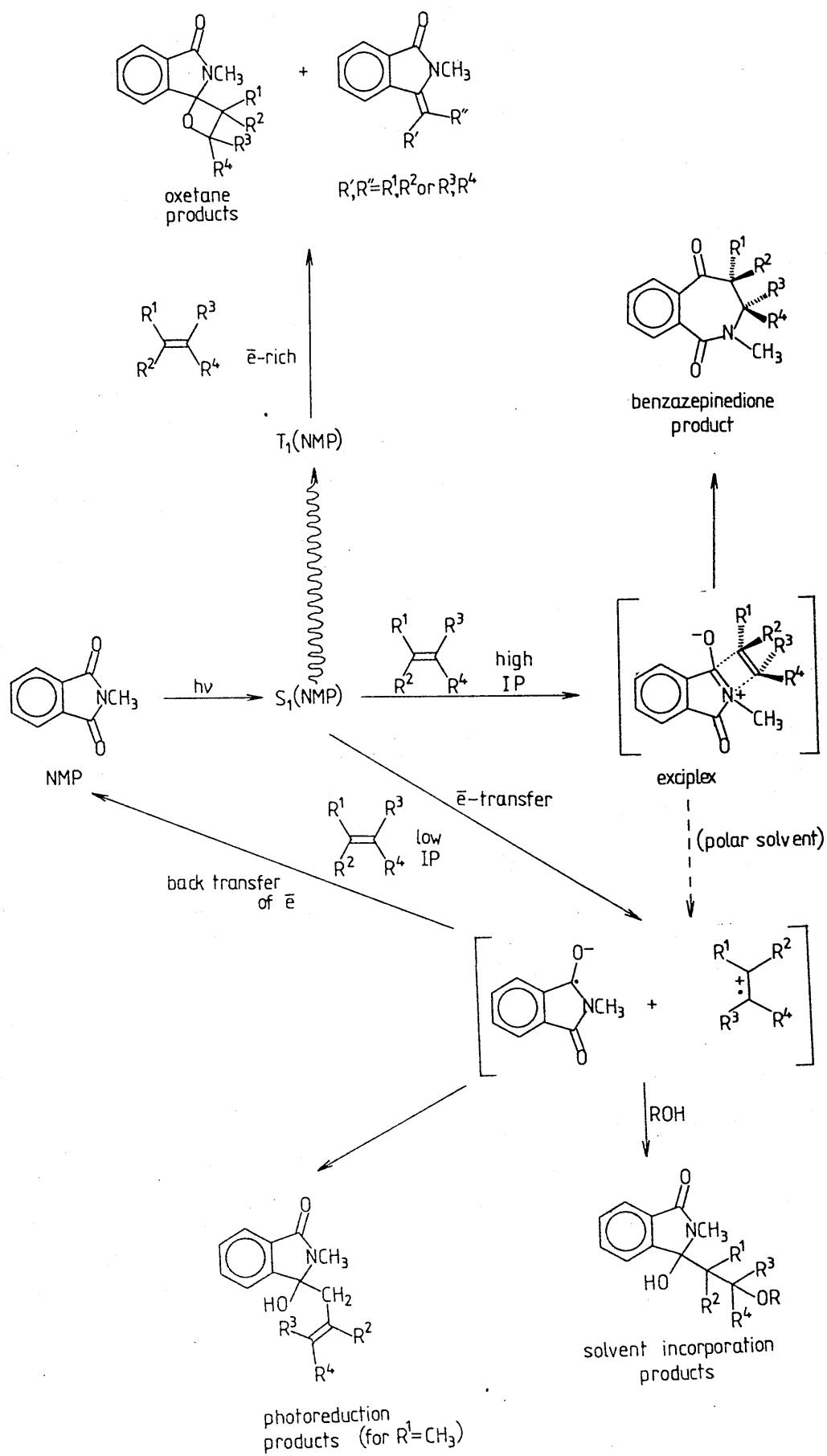


Some tri- and tetrasubstituted alkenes appear unreactive towards excited *N*-methylphthalimide in acetonitrile solution; Mazzocchi⁴⁹ has suggested that in these circumstances the radical ion pair is unreactive and back-transfer of the electron occurs. In the presence of a hydroxylic solvent the formation of solvent incorporation products is also observed. This has recently been investigated further by Maruyama and Kubo⁵¹; one such reaction is the reaction of *N*-methylphthalimide with 1,1-diphenylethene (43). It is also proposed⁵¹ that the exciplex (which leads to benzazepinedione) may

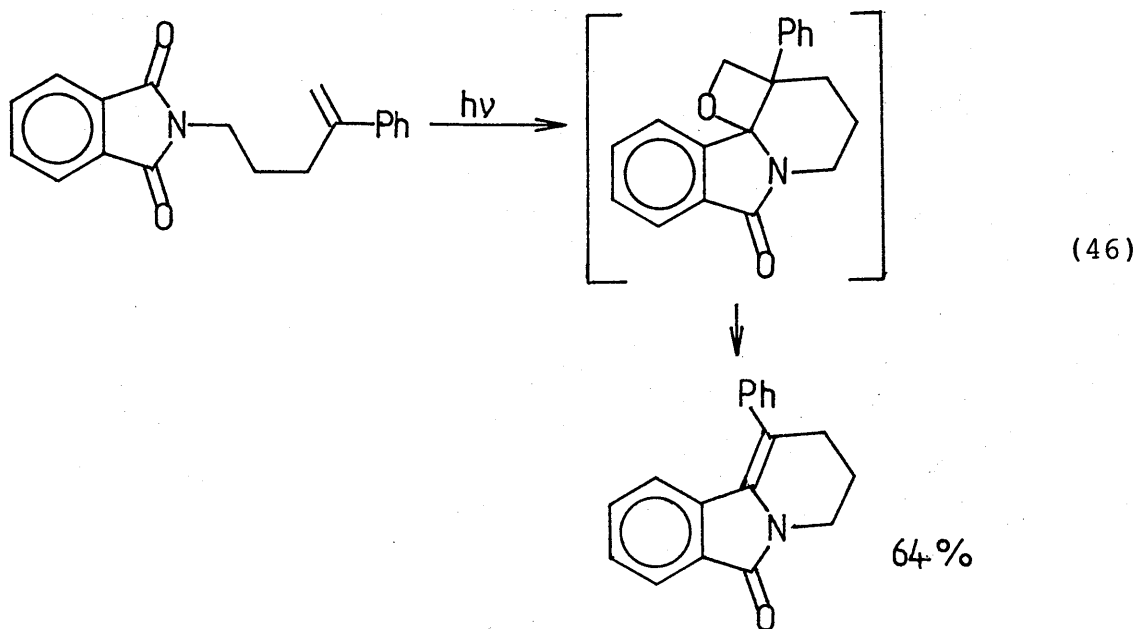
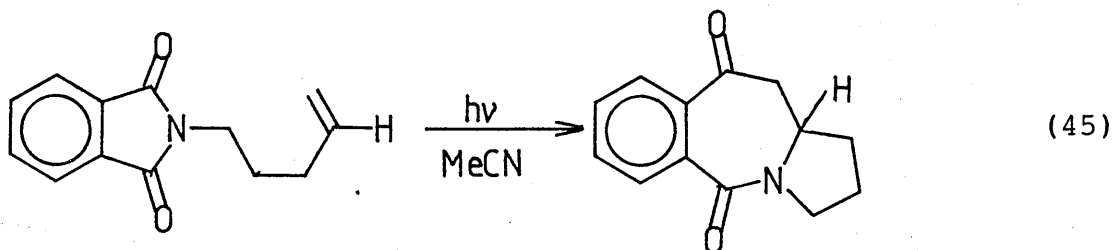
dissociate into radical ions in polar solution, and this too influences the product formation.

An overall scheme is presented (44), showing the competing reactions which may occur for the reaction of N-methylphthalimide with an alkene, summarising the factors which lead to the formation of the various products.

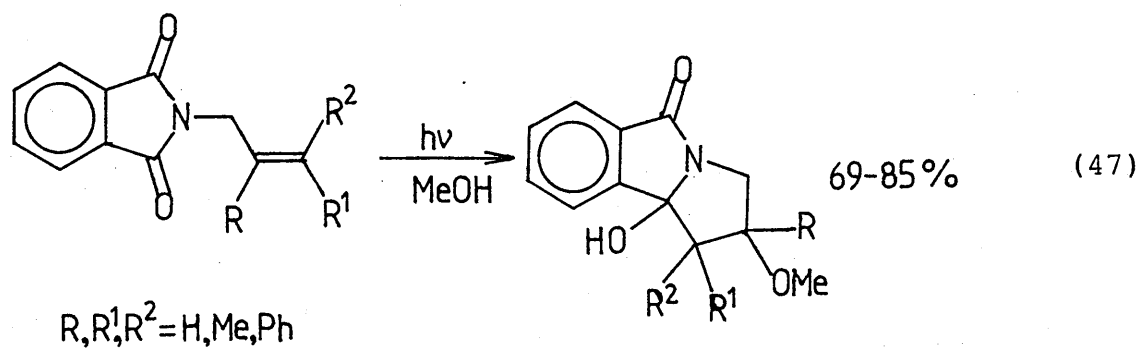




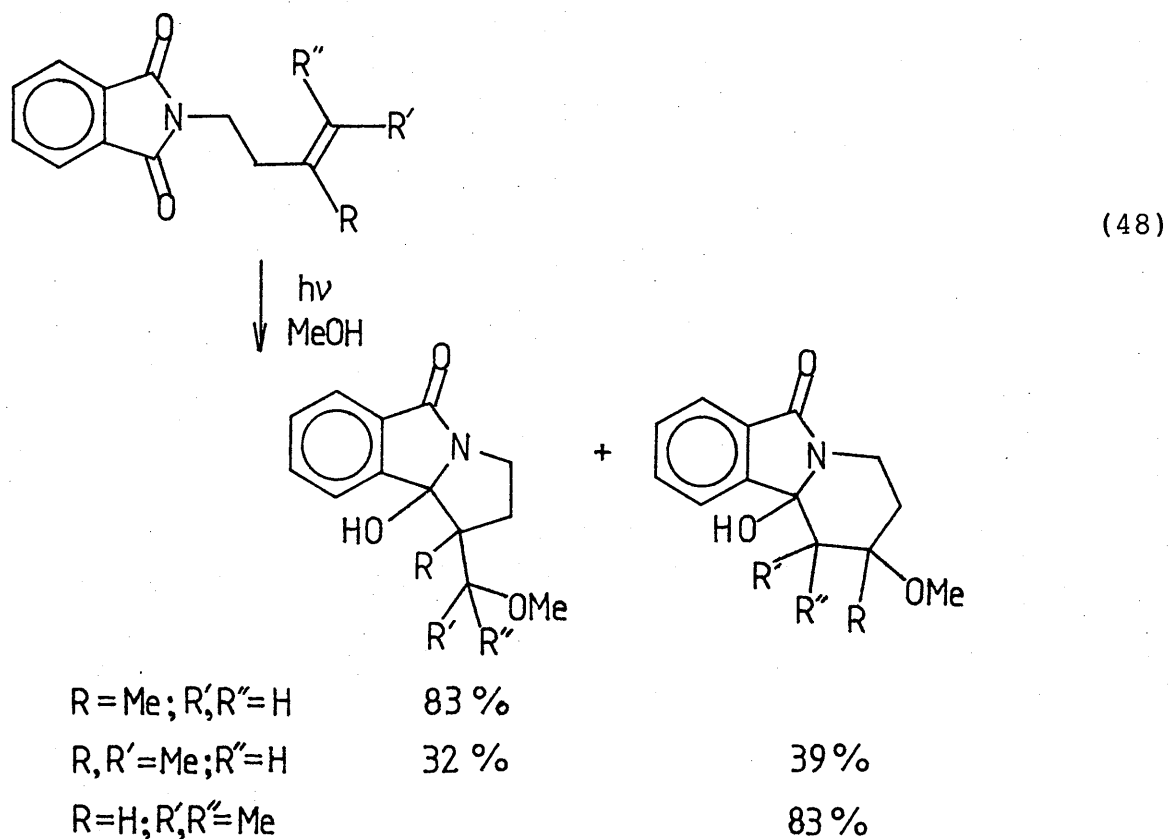
As with the hydrogen abstraction reactions, the photocycloaddition reactions can be extended to intramolecular examples; one such is the reaction of N-(4-pentenyl)phthalimide (45)⁴⁸. The results of these intramolecular reactions are comparable with those of the intermolecular reactions, including the appearance of an oxetane-derived product from the electron-rich N-(4-phenyl-4-pentenyl)phthalimide (46)⁴².

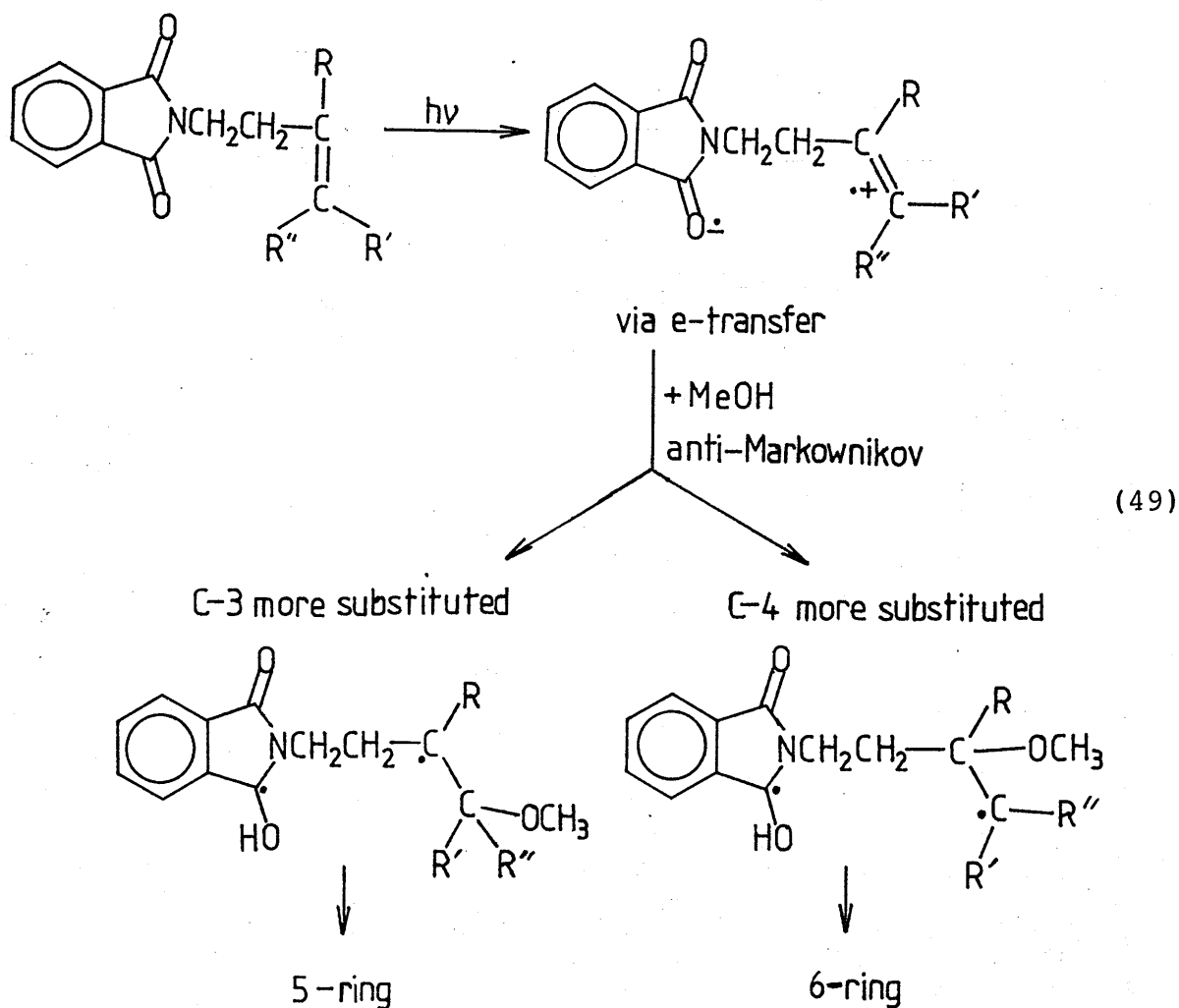


Irradiation of N-(2-alkenyl)phthalimides gives alkene addition products with solvent incorporation in methanol (47)^{52,53}, and no products (excepting those of cis-trans isomerisation about the alkene double bond) in acetonitrile⁵⁴. These reactions are postulated to be via radical ions formed from an initial electron transfer.

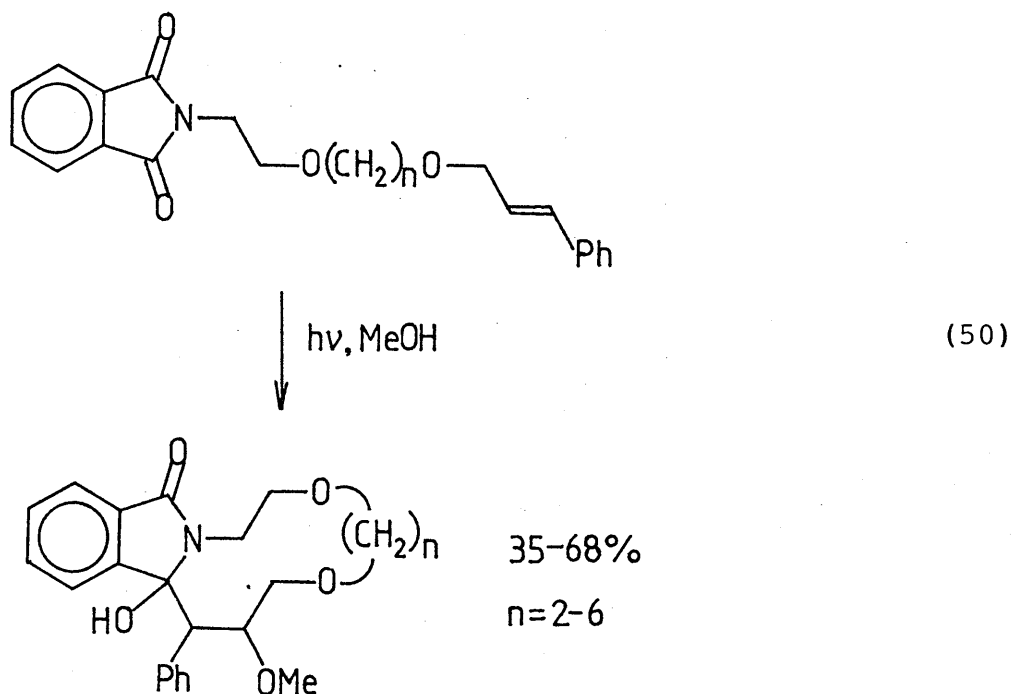


For N-(but-3-enyl)phthalimides there is competition between the formation of five-membered or six-membered rings (48)⁵⁵. The product distributions are accounted for by the effects of methyl groups in stabilising the intermediate radical centres (49).





As with the intramolecular hydrogen abstraction reactions, this intramolecular electron-transfer photocycloaddition solvent incorporation reaction may be extended to yield macrocyclic products with ring sizes of up to fifteen (50)^{56,57}.



Thiocarbonyl photochemistry

Although it had been recognised for many years that thiocarbonyl compounds were photochemically active, it was not until the late 1960's that detailed investigations were started. Although most of the earlier work was carried out on thioketones, the photochemistry of other thiocarbonyl compounds such as thioesters, thioparabanates, thioureas and thiocarbonates has also been studied. More recently, work has been carried out on thioamides and thiomides. The subject has been reviewed several times in the past ten years⁵⁸⁻⁶², and a further review is due to be published soon⁶³.

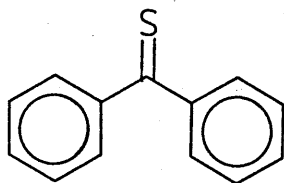
Excited states

The photochemistry of thiocarbonyl compounds is mainly concerned with three excited states: the first excited singlet (n, π^*) state, the first excited triplet (n, π^*) state, and the second excited singlet state. In the case of the thioketones this latter state has been established as (π, π^*),

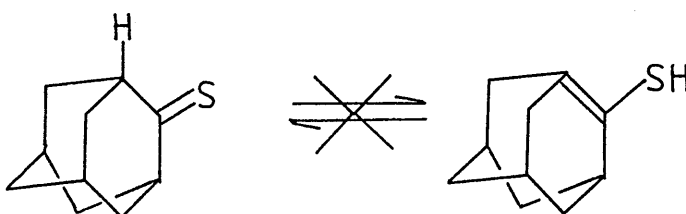
and its energetic accessibility and lifetime cause it to make a significant contribution to the photochemistry; this is one of the most interesting features of thioketones - the violation of Kasha's rule⁸. The photophysics of thiocarbonyl compounds have been reviewed in a general article on wavelength-dependent photochemistry⁶¹ and in a thorough and extensive discussion by Steer⁶⁴.

Ground state

Thioketones and thioaldehydes are not all stable in the ground state with respect to polymerisation, and for this reason only a limited range is available at room temperature. The only known stable thioaldehyde is 2,4,6-tri-*t*-butylthio-benzaldehyde⁶⁵, which relies on the steric crowding to inhibit reaction. The stable thioketones have no α -hydrogen (e.g. thiobenzophenone (51)), or have geometric constraints such that tautomerisation to the enethiol is prevented (e.g. adamantanethione (52)). However, if the thiocarbonyl group is stabilised by an adjacent electronegative atom then the compound is relatively stable and may be handled easily at room temperature, e.g. thioureas, xanthates, thioamides and thioimides.



(51)



(52)

Thiocarbonyl compounds are planar about the carbon-sulphur double bond. The thiocarbonyl bond has been shown to be less polar than the carbonyl bond by dipole moment measurements⁶⁶, supported by SCF and CI calculations⁶⁷. In the ground state the HOMO is the n orbital of the sulphur. For simple thiocarbonyl compounds the electrons in this orbital are calculated to be more highly localised on the sulphur atom than the electrons in the analogous carbonyl compound are localised on the oxygen atom⁶⁷. The second highest occupied molecular orbital in the ground state is the π orbital of the thiocarbonyl bond in most cases. However the order of the n_s and π_{cs} orbitals may be reversed in some compounds, e.g. imidazoline-, thioazoline- and oxazoline-2-thiones⁶⁸. The ground state chemistry of thiocarbonyl compounds has been well investigated and reviewed⁶⁹.

First excited singlet state

Many workers⁷⁰⁻⁷³ have measured the electronic absorption spectra of thiones in solution. Several absorption bands can be observed, of which the lowest-energy transition is in the visible region and accounts for the colour of the compounds. This transition has been assigned to an electric-dipole forbidden $n \rightarrow \pi^*$ electron promotion. Huber and co-workers⁷⁴ have suggested that in aromatic thiones there is a mixing of n and π^* orbitals which leads to an increase in intensity of the ($n \rightarrow \pi^*$) transitions, via an overlap of ring π orbitals with the n_s orbital.

The spectra of large thiones in solution show little resolvable structure at room temperature. However, it can be seen that the absorption maxima of aromatic thiones generally

lie at longer wavelengths than those of aliphatic thiones, because the extended conjugation lowers the π^* orbital energy. The higher energy of the $n \rightarrow \pi^*$ transition of thioureas⁷⁰, thioamides^{71(b)} and other such thioacid derivatives is likely to be due to the conjugation of the heteroatom lone pairs with the thiocarbonyl moiety. Table 1.1 shows some of these differences.

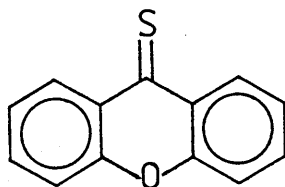
Thiocarbonyl compound (solvent)	$S_0 \rightarrow S_1$ (n, π^*)			Reference
	λ_{\max} (nm)	E (kJ mol ⁻¹)	ϵ (l mol ⁻¹ cm ⁻¹)	
Thiocamphor	493	243	12	71(a)
Thiobenzophenone (hexane)	609	196	184	73(c)
Dithiosuccinimide (ethanol)	402	298	135	75
<u>N</u> -Methylthiobenzamide (heptane)	402	298	302	76

Table 1.1: Some typical values for S_1

In thiocarbonyl compounds the S_1 - T_1 zero-point energy differences are small, suggesting that there is only a relatively weak interaction between the two unpaired electrons; thus both S_1 and T_1 would be expected to show biradical character⁷⁷.

The excited state decay dynamics for the S_1 state have only been studied in detail for small thiocarbonyl compounds, although general principles are known for larger molecules. For these latter, intersystem crossing to T_1 is more efficient than radioactive decay from S_1 : as a result

fluorescence from S_1 is not observed. There are many vibronic states in T_1 which are equienergic with the populated S_1 levels, and intersystem crossing is a rapid process for which quantum efficiencies have been shown to be close to unity⁷⁸⁻⁸⁰. In the case of xanthione (53) the lower limit for the rate constant of $S_1 \rightsquigarrow T_1$ intersystem crossing has been calculated to be in excess of 10^{11} s^{-1}



(53)

This rapid intersystem crossing means that in these larger molecules, excitation to S_1 leads only to emission from T_1 ^{74,79,81,82}. Another consequence is that few chemical reactions are seen to occur from S_1 ; the only known examples are the hydrogen abstraction reactions of certain thiobenzoyl derivatives of aromatic hydrocarbons⁸³ and the fragmentation reactions of dithiolactones⁸⁴.

First excited triplet state

The lowest energy electronic transition in the majority of thiocarbonyl compounds is a spin-forbidden triplet $n \rightarrow \pi^*$ electron promotion. Such transitions lie at lower energy than those for the corresponding carbonyl compounds, which is in accordance with the involvement of a 3p electron rather than a 2p electron. Direct absorption gives weak absorption bands in the electronic spectrum, which are overlapped by the bands of the spin-allowed singlet $n \rightarrow \pi^*$ absorption system⁸¹. The oscillator strength for direct absorption is often only a factor of about 10 smaller than that of the corresponding $S_0 \rightarrow S_1$ absorption⁸⁵. Some typical T_1 energies are given in Table 1.2.

Thiocarbonyl compound	T_1 (n, π^*)	Reference
	E (kJ mol ⁻¹)	
Thiofenchone	214	81
Thiobenzophenone	159	79
Thiophosgene	209	85
<u>N</u> -Methylthioacridone	179	86

Table 1.2: Triplet state energies of thiocarbonyl compounds

The triplet state may also be populated by intersystem crossing from the S_1 (n, π^*) state; the triplet quantum yield is about 0.8 - 1.0⁸⁷.

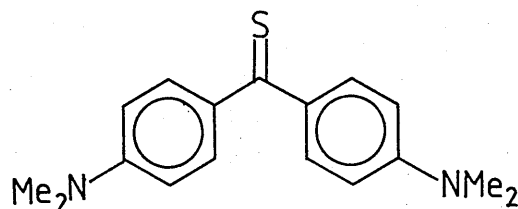
Depopulation of the triplet state occurs via several mechanisms. The phosphorescence emission spectra and quantum yields for some thiocarbonyl compounds have been measured; some typical data are presented in Table 1.3. It is also a striking feature of thiocarbonyl photochemistry that aromatic thioketones such as thiobenzophenone show phosphorescence at room temperature⁸⁸. The low quantum yields, even at 77 K, suggest that the primary decay processes are non-radiative, of which the most important is intersystem crossing to the ground state. Chemical fragmentation of the thiocarbonyl compound is not a major decay route, and the quantum yield which has been measured for the photodecomposition of xanthione is minimal⁸⁹. One other type of decay process is chemical reaction, and there are many known examples of thiocarbonyl photoreactions which occur from this T_1 (n, π^*) state.

Thioketone	τ (μ s)	ϕ_p	Reference
Thiobenzophenone	25	0.021	74
Xanthione	40	0.11	74
Adamantanethione	110	-	81

Table 1.3: Thione phosphorescence in hydrocarbon glass at 77 K

In fluid solution there may be triplet decay by quenching using added triplet quenchers^{78,88-91}. If the triplet energy of the quencher is lower than that of the donor thione, then the process is diffusion-controlled. One such quencher is oxygen; quenching leads to the formation of singlet oxygen. Self-quenching may also occur as a triplet decay process: this phenomenon ($T_1 + S_0 \rightarrow 2S_0$) is observed at concentrations as low as 10^{-5} M⁸⁹, and it competes with intramolecular decay processes. The rate constant for self-quenching is diffusion-controlled. It has been proposed that the self-quenching may occur via a triplet excimer⁸⁹ which then decays non-radiatively to form two ground-state molecules. Although evidence has been found for an excimer of this type in the case of Michler's thione (54)⁸¹, the excimer phosphorescence has proved elusive in other cases⁹². If self-quenching does occur via excimer formation, then the efficient self-quenching of thiocarbonyl relative to carbonyl compounds may be accounted for by spin-orbit coupling of the low-lying excimer triplet to its unbound ground state. Studies involving quenching of an excited state thione by a variety of different ground state thiones⁹² support the idea that the n orbital of the ground state thioketone chromophore acting as the donor is involved in the quenching process, on the basis that thiones substituted with sterically bulky or electron-with-

drawing groups are less efficient quenchers than those substituted with electron-donating groups.



(54)

It has been proposed that the lowest triplet state of thiocarbonyl compounds in which $E(S \rightarrow S_2) - E(S \rightarrow S_1) < 72 \text{ kJ mol}^{-1}$, such as thiobenzamides, may be (π, π^*) ⁹³.

Second excited singlet state

Several strong transitions are seen in the UV spectra of thiocarbonyl compounds, but these cannot all be assigned. However in the cases of some thioacid derivatives⁷⁰, and aromatic thiones, the $S_0 \rightarrow S_2$ transition can be described as $\pi \rightarrow \pi^*$. The energy of the (π, π^*) states is slightly less for compounds in which the thiocarbonyl π orbital is conjugated. Table 1.4 gives some typical values.

Thiocarbonyl compound (solvent)	$S_0 \rightarrow S_2 (\pi, \pi^*)$			Reference
	λ_{max} (nm)	E (kJ mol ⁻¹)	ϵ (l mol ⁻¹ cm ⁻¹)	
Thiobenzophenone (hexane)	314.5	380	17,800	73(c)
Thiocamphor	244	244	11,500	71(a)
Dithiosuccinimide (ethanol)	321	373	14,400	75
<u>N</u> -Methylthiobenzamide (heptane)	288	415	6,500	76

Table 1.4: Some typical values for S_2

Studies on xanthione have shown that the $S_0 \rightarrow S_2$ transition leads to substantial charge transfer from the sulphur atom to the adjacent carbon atom, and the energy of this transition may be altered slightly by substituents on the aromatic ring⁹⁴ which is conjugated to the thiocarbonyl group. Comparison with xanthone shows that the changes in energy for the $S_0 \rightarrow S_2$ transition are more affected by substituents on the aromatic ring, indicating that the electron density change for the transition is more evenly distributed throughout the whole conjugated system than in xanthione.

Decay may occur from the $S_2(\pi, \pi^*)$ excited state by fluorescence, by radiationless decay or by chemical reaction. The lifetimes of the $S_2(\pi, \pi^*)$ states of thiocarbonyl compounds are short: at 295 K that of xanthione in benzene is 18 ps⁹⁵, and those of xanthione and thioxanthione in perfluoroalkane solvents are 175 ps and 64 ps respectively⁹⁶.

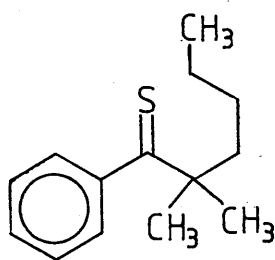
$S_2 \rightarrow S_0$ fluorescence has been observed for some, but not all, larger organic thiones^{79,96}, and the radiative rate constants are in agreement with the theoretical values calculated from the oscillator strength⁹⁷. Intramolecular radiationless internal conversion is a major decay pathway from S_2 ; if it is assumed that radiationless decay is irreversible, then a rate constant for it can be calculated from the rates of radiative and overall decay. The rate constants calculated in this way are smaller than those of the oxygen analogues; the reason for the smaller value cannot be directly related to $S_2 \rightsquigarrow S_1$ internal conversion. A recent paper⁹⁶ concerning decay from S_2 in a variety of thiones concludes that intramolecular $S_2 \rightsquigarrow S_1$ internal conversion dominates S_2 decay in inert perfluoroalkane solvents, but

that in more strongly interacting solvents the dominant processes are intermolecular - either photochemical or photo-physical. Some values for the radiative and non-radiative decay from the $S_2(\pi, \pi^*)$ states of thiocarbonyl compounds are given in Table 1.5.

Quenching of S_2 by singlet quenchers is known⁹⁸, and decay of the S_2 state by self-quenching has also been observed, having first been noted for thiobenzophenone⁹⁹.

Thiocarbonyl compound (solvent)	$\phi_f \times 10^3$	$k_R \times 10^{-7}$ (s^{-1})	$k_{NR} \times 10^{-16}$ (s^{-1})	Reference
Arylalkylthione (55) (n-hexane)	4.4	1.1	0.24	98
Xanthione (perfluoroalkane)	14	8.0	5.7	96
Thioxanthione (perfluoroalkane)	2.3	3.6	160	96
Xanthione (benzene)	1.2	6.7*	5.6*	95

*calculated from oscillator strength

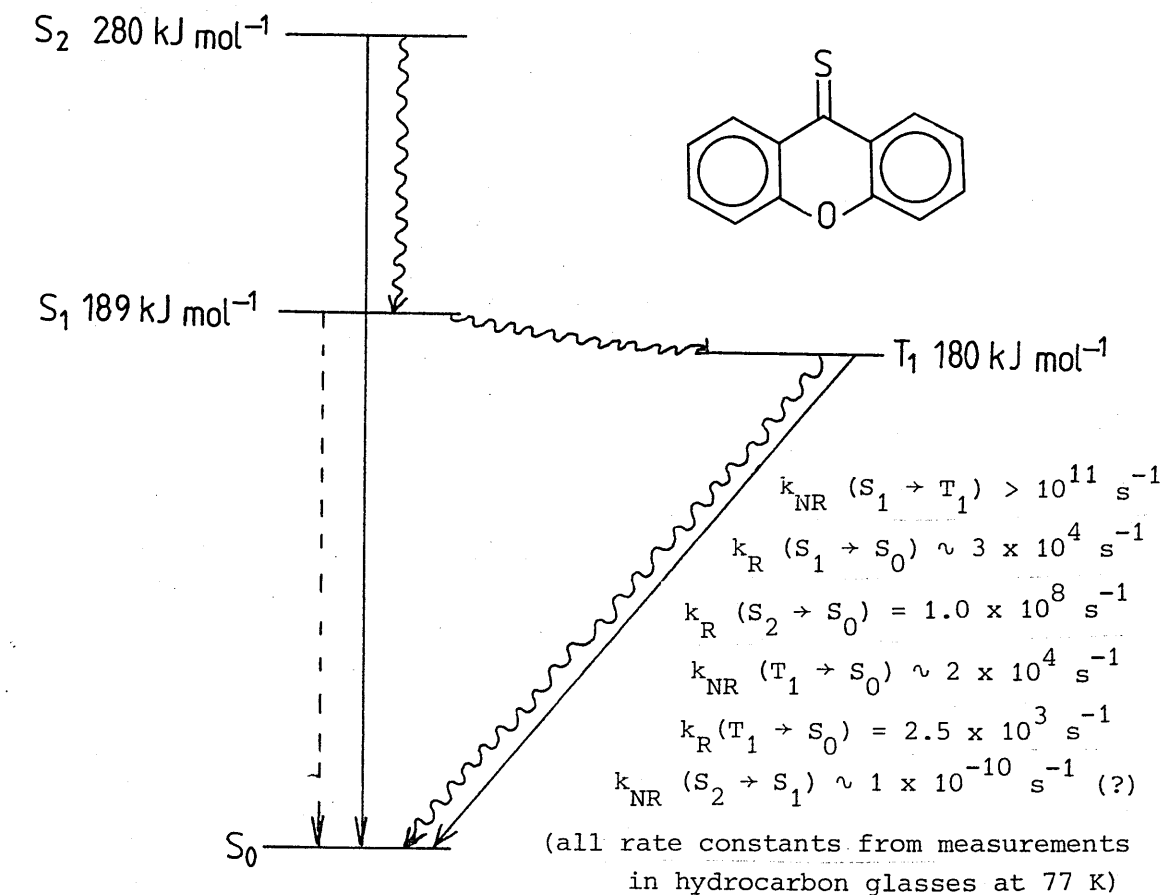


(55)

Table 1.5: Some values for radiative and non-radiative decay from the S_2 state of thioketones at 295 K

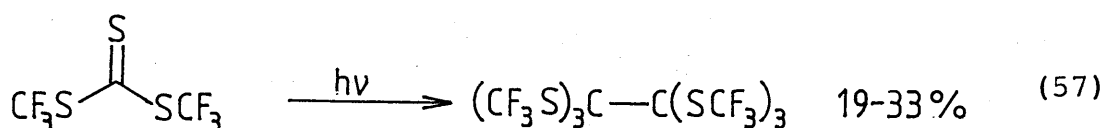
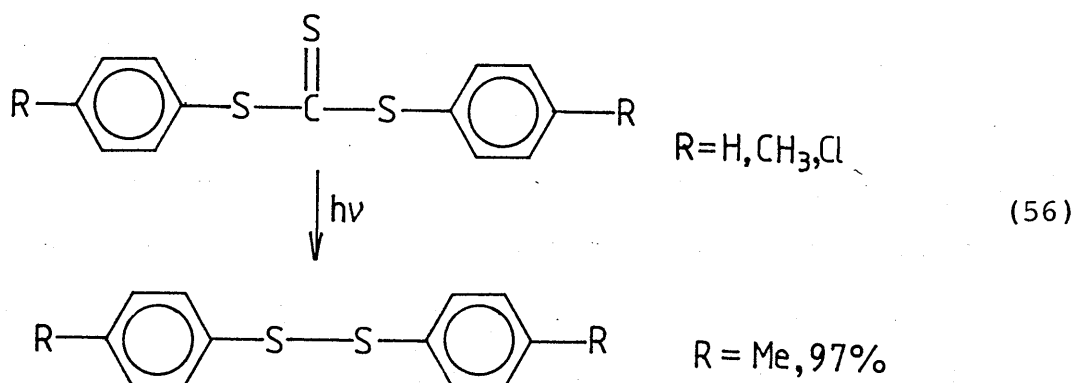
A Jablonski diagram for xanthione⁶⁴ provides a useful summary of thioketone photophysics.

Jablonski diagram for xanthione

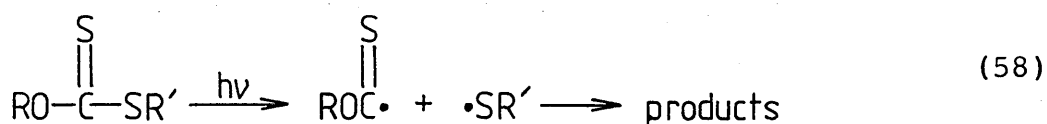


Fragmentation and rearrangement

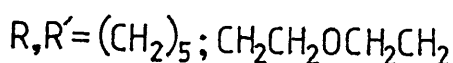
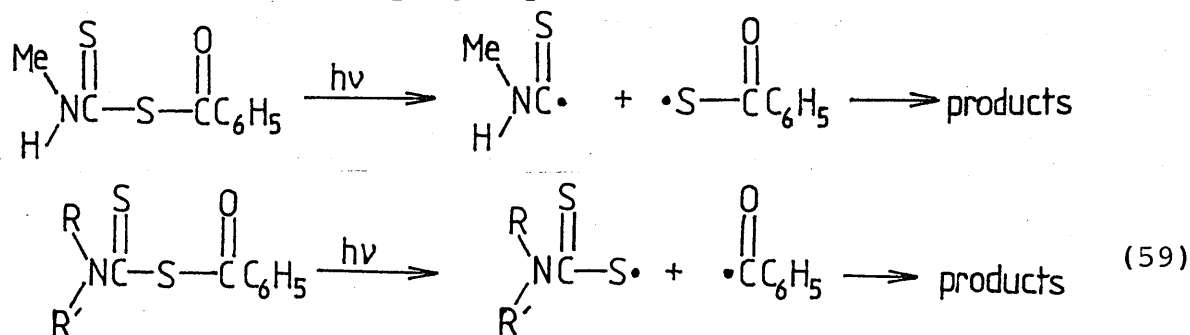
Ketones and related carbonyl compounds undergo a number of photochemical reactions in which the first step is cleavage of the α -C-C bond. However such reactions are not generally observed for thiocarbonyl compounds because the lower energy of the thiocarbonyl excited state makes cleavage of an adjacent bond less favourable energetically⁶³. Consequently the pattern of α -cleavage reactions which emerges is that a relatively weak α -C-S bond can easily be cleaved (e.g. as in S-alkyldithioesters), the stronger α -C-O or α -C-N bond can occasionally be broken, and the strong α -C-C bond is only broken in exceptional cases. One example of cleavage of an α -C-S bond is the fragmentation of diaryl trithiocarbonates to form disulphides (56)¹⁰⁰. Another α -C-S cleavage occurring to give a different type of product is that in bis(trifluoromethyl) trithiocarbonate, which gives hexakis(trifluoromethyl)-ethane (57)¹⁰¹.



Simple xanthates also show cleavage of the α -C-S bond in preference to cleavage of the α -C-O bond. This explains product formation from O-ethyl-S-benzyl xanthate¹⁰² and also from O-alkyl-S-methyl xanthates (58)¹⁰³.

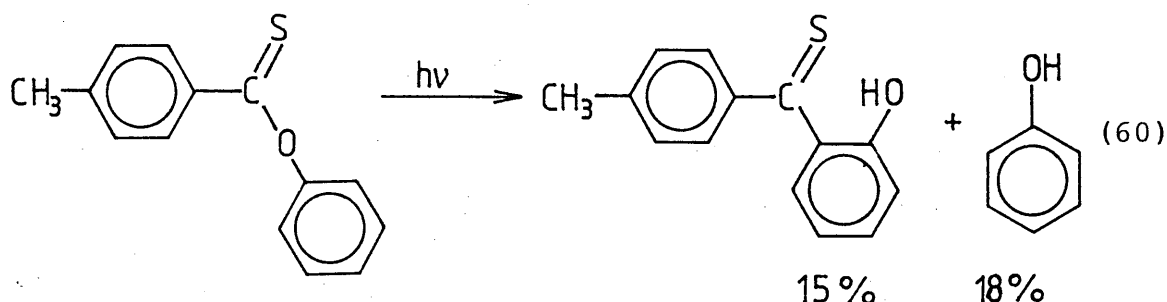


Dithiocarbamic acid derivatives in which there is one alkyl substituent on the nitrogen atom show cleavage of the α -C-S bond rather than the α -C-N bond¹⁰⁴; however, in cases where there are two alkyl substituents on the nitrogen atom the C-S bond which is broken is β to the thiocarbonyl group, but α to the carbonyl group (59)¹⁰⁵.

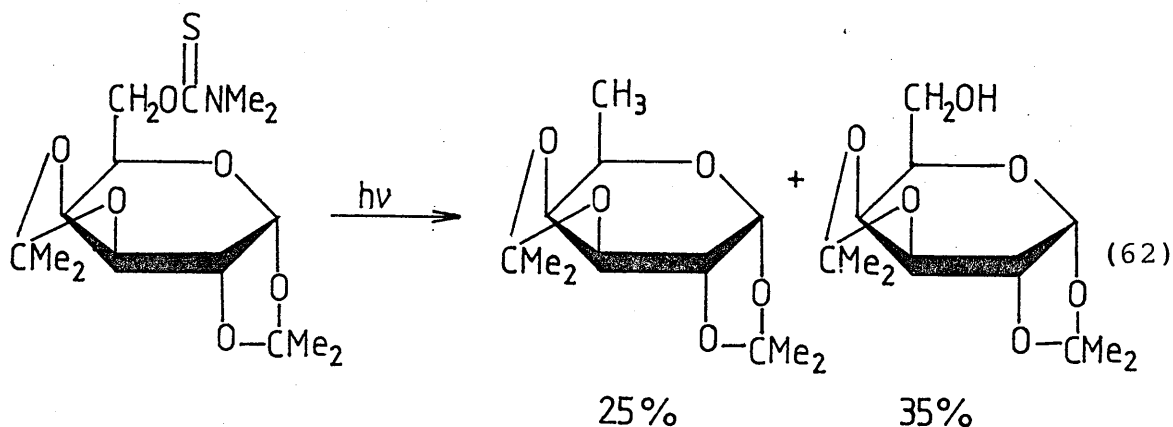
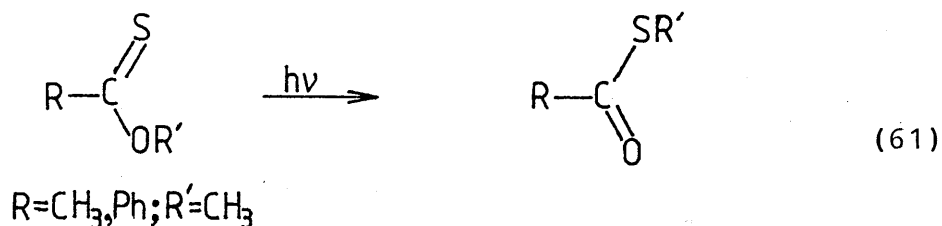


Cleavage of an α -C-O bond is also known, although there are fewer examples of this than of α -C-S cleavage.

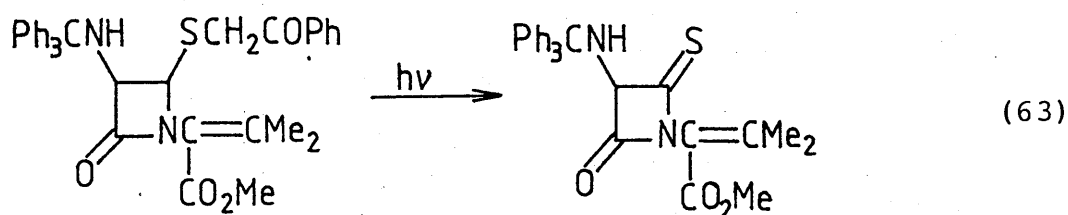
Irradiation of an O-aryl thioester yields rearrangement products which can be accounted for by α -cleavage in a reaction parallel to the photo-Fries reaction of aryl carboxylates (60)¹⁰⁶.



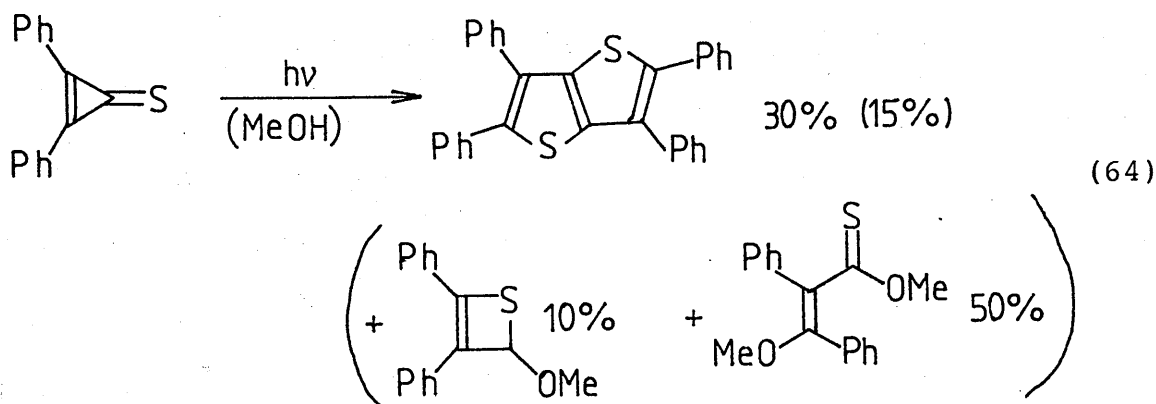
However for O-alkyl thioesters the preferred reaction is a rearrangement to the S-alkyl thioester; this is a 1,3-shift which is formally a β -cleavage (61)¹⁰⁶. There are also competing photocycloaddition reactions which will be discussed later. A similar 1,3-shift has been proposed for the photolysis of dimethylthiocarbamates as a route to deoxy-sugars (62)¹⁰⁷.



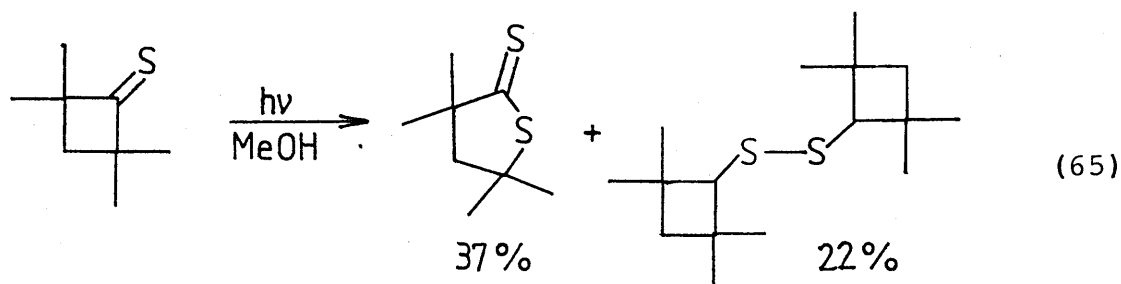
Very little evidence exists for α -cleavage of a C-N bond; the only case in which it might happen is the photolysis of N-phenylthiourethane, which gives aniline among the products, but this reaction is far from being 'clean'¹⁰⁸. Another indication of the stability of the α -C-N bond to cleavage is in the photochemical preparation of the thioimide (63) which does not easily undergo further breakdown¹⁰⁹. Thiosuccinimides and thiophthalimides have recently been reported to be resistant to α -cleavage upon irradiation¹¹⁰.



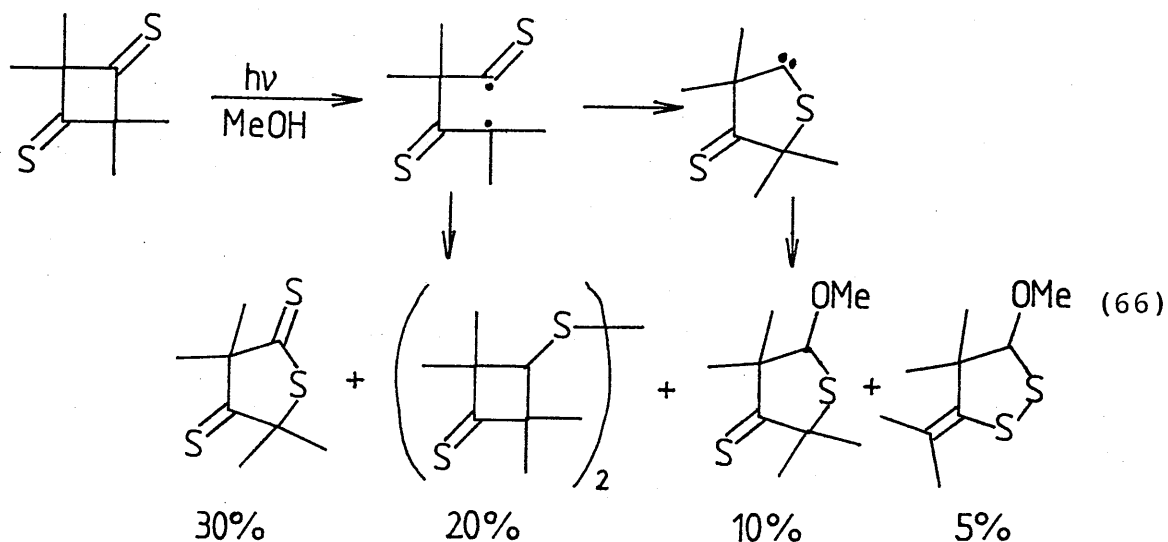
α -Cleavage of a C-C bond can be achieved in strained systems, where excitation energy is supplemented by the strain energy, thus allowing bond breakage to occur. Diphenylcyclopropenethione is one such example¹¹¹, giving thieno[3,2-c]thiophene as the only product in the absence of methanol¹¹², but in its presence the additional products are a 4-methoxythiete, which is formed via a cyclic carbene, and a 3-methoxythioacrylate, which is formed via a ring-opened carbene. This latter product requires an oxidation process during its formation (64).



Cyclobutanethiones have been well studied for their α -C-C cleavage reactions, which are known to occur from the (n, π^*) triplet state. The photolysis of 2,2,4,4-tetramethylcyclobutanethione gives rise to an α -cleavage product together with a photoreduction product¹¹³. The mechanism of formation of the thiolane-2-thione is uncertain, but the authors suggest that it may result from the trapping of a ring-opened biradical by a ground state thione molecule (65).



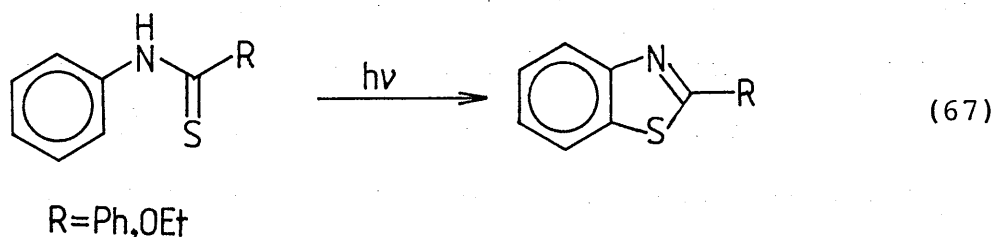
Cyclobutane-1,3-dithiones give analogous products upon irradiation, together with solvent incorporation products which arise from the reaction of methanol with an α -thia-carbene, formed from an initial 1,4-biradical (66).



Cyclisation reactions

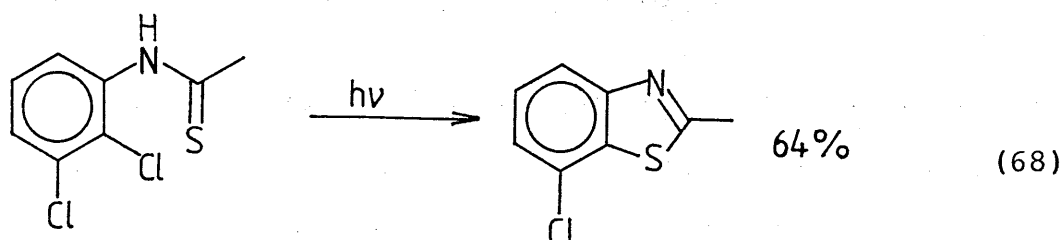
Those overall cyclisation reactions which involve hydrogen abstraction or photocycloaddition will be discussed later. The cyclisation reactions described here do not

readily fall into either of those categories but they are of synthetic utility and mechanistic interest. N-Phenylthio-benzamide (67, R = Ph) cyclises oxidatively to form 2-phenyl-benzothiazole; the authors do not propose any mechanism (67)¹¹⁴.

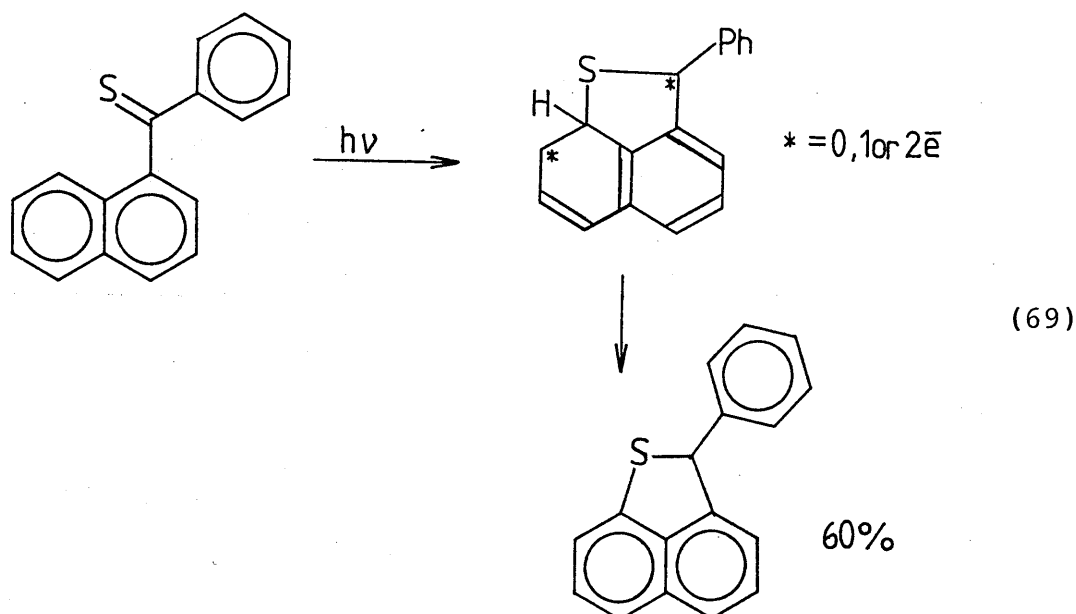


Similarly N-phenylthiourethane (R = OEt) undergoes cyclisation as well as cleavage (discussed above) upon irradiation¹⁰⁸; in this case it is necessary for oxygen to be present.

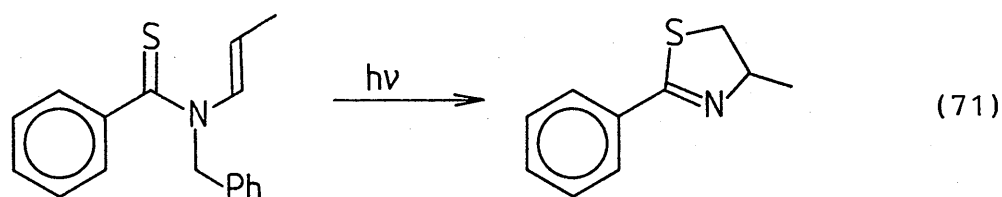
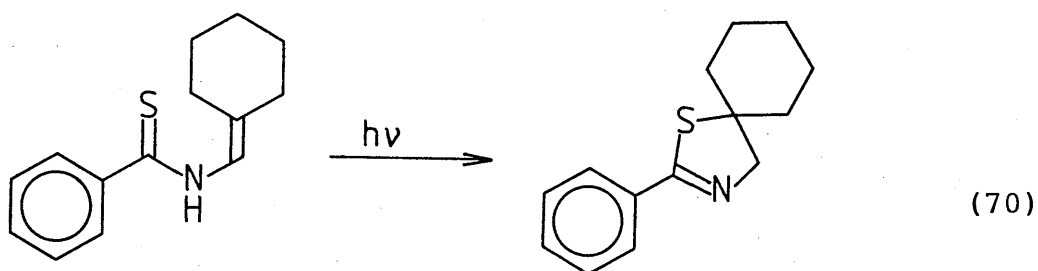
Elimination of hydrogen halide is seen in the photocyclisation of the N-thioacetyl-2-haloanilines¹¹⁵. The halogen atom which is lost must be in the ortho position, and bromine is eliminated more easily than chlorine (68).



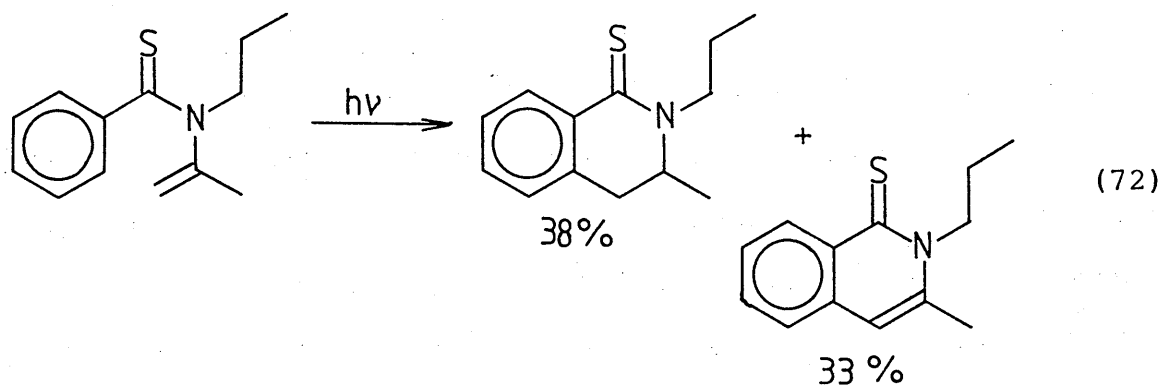
One especially interesting non-oxidative photocyclisation is that of the phenyl arylthioketones, in which the aryl group is a polycyclic aromatic group such as 1-naphthyl⁸³. This reaction appears to proceed from the $S_1(n, \pi^*)$ state, and is thought to involve a dipolar intermediate.



The photocyclisation of thioenamides has also received attention¹¹⁶. N-Vinylthiobenzamide systems undergo a non-oxidative cyclisation (70). The N-benzylated derivatives give similar products (71)¹¹⁷, in a reaction that includes a debenzylation step. It is proposed that this debenzylation might be an early step in the reaction.

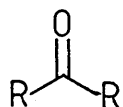


With alkyl substituents on the nitrogen the products include an isoquinoline-1-thione and a dihydroisoquinoline-1-thione. It is likely that this reaction involves a six-electron electrocyclic ring closure followed by a thermal 1,5-hydrogen shift. The mechanism of oxidation to the isoquinoline-1-thione is unknown¹¹⁷.

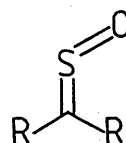


photooxidation

It has long been known that thiocarbonyl compounds are subject to photooxidation. Some thioketones, such as thio-benzophenone, are thermally oxidised in air¹¹⁸, and light increases the overall rate of oxidation. Other thioketones, such as 9-xanthione, only react in the presence of light, and some, such as 4-thioflavone, are not oxidised even upon irradiation¹¹⁹. In most cases the irradiation products include sulphur and sulphur dioxide together with either the ketone (73) or the sulphine (74) or both. However some thioamides lead to products in which the thiocarbonyl sulphur has been raised to an even higher oxidation state.



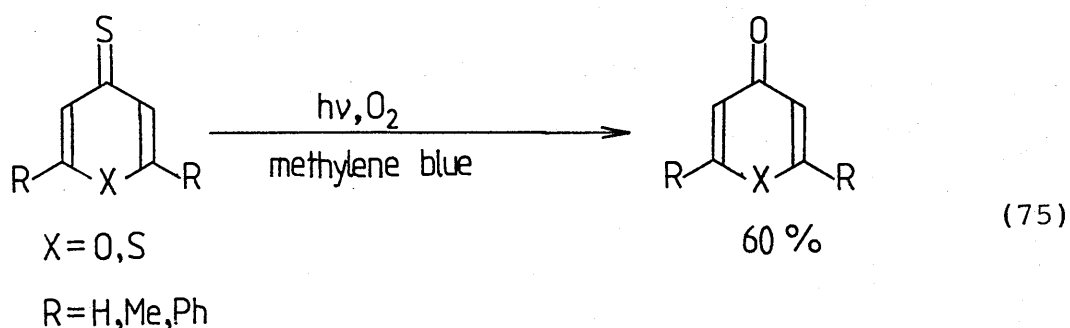
(73)



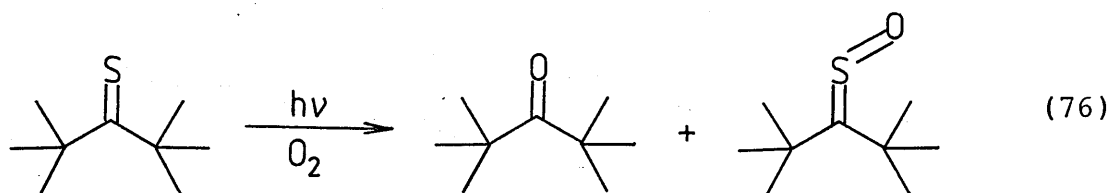
(74)

In all of the cases for which the mechanism has been studied the reaction is known to proceed from the $T_1(n, \pi^*)$ state of the thioketone. It is thought that the triplet thiocarbonyl may act as a singlet oxygen sensitiser by reacting with a molecule of ground state oxygen to produce a molecule of singlet molecular oxygen and the ground state thiocarbonyl¹²⁰. The rate of quenching of the $T_1(n, \pi^*)$ state of xanthione by ground state oxygen⁸⁹ is $3.7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

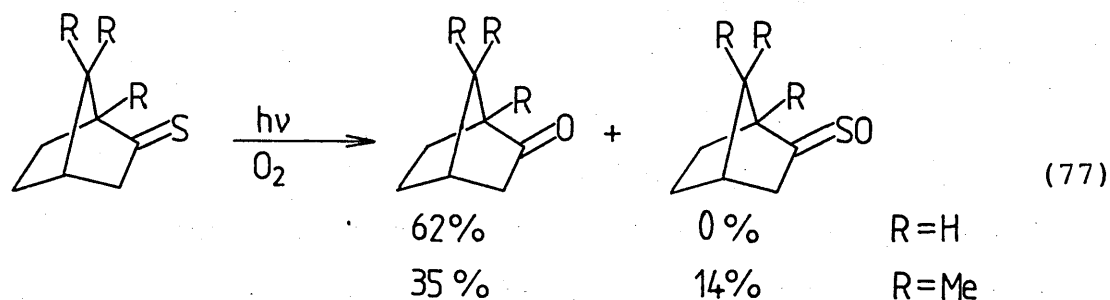
The idea of involvement of singlet oxygen is also supported by the fact that the reaction is sensitised by dyes which are known to generate singlet oxygen (75)¹²¹ and inhibited in the presence of singlet oxygen quenchers. The efficiencies of singlet oxygen production of several thioketones were measured by following the bleaching of 1,3-diphenylisobenzofuran in chloroform¹²²: the efficiencies at 0.01 M thione concentration were ~ 0.7 . Rate constants for the quenching of singlet oxygen by a series of thioketones were measured by monitoring the inhibition of the self-sensitised photooxidation of rubrene¹²³: the rate constants were $\sim 1 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ at the experimental concentration. This work also suggested that direct physical quenching of singlet oxygen by thioketones was not an important process; this conclusion was drawn from a study of the effect of thioketone concentration upon the quantum yield of oxidation.



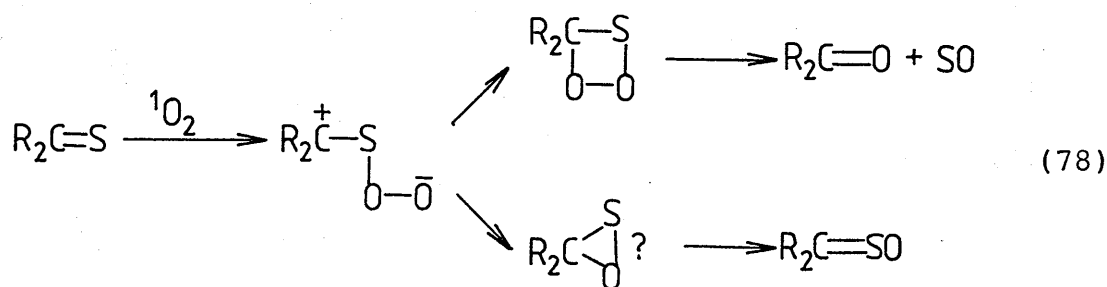
A number of factors affect the formation of sulphine or ketone as the major product. Sulphine formation was first observed for di-t-butyl thioketone (76)^{124,125}, where it is the major product in polar solvents; the ketone is the major product in non-polar solvents. The ketone formation was found to be barely affected by the addition of singlet oxygen quenchers¹²⁴, and it seems possible that it may arise by an additional route not involving singlet oxygen.

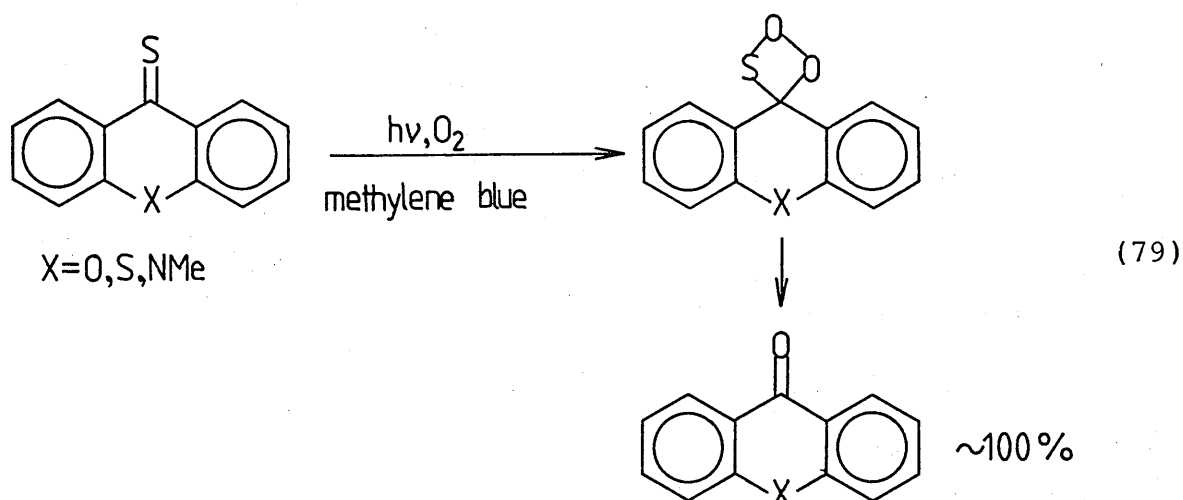


Steric effects also influence the reaction. The ratios of ketone to sulphine formed by norbornane-2-thione (77, R = H) and thiocamphor (77, R = Me) provide a nice example¹²⁶.

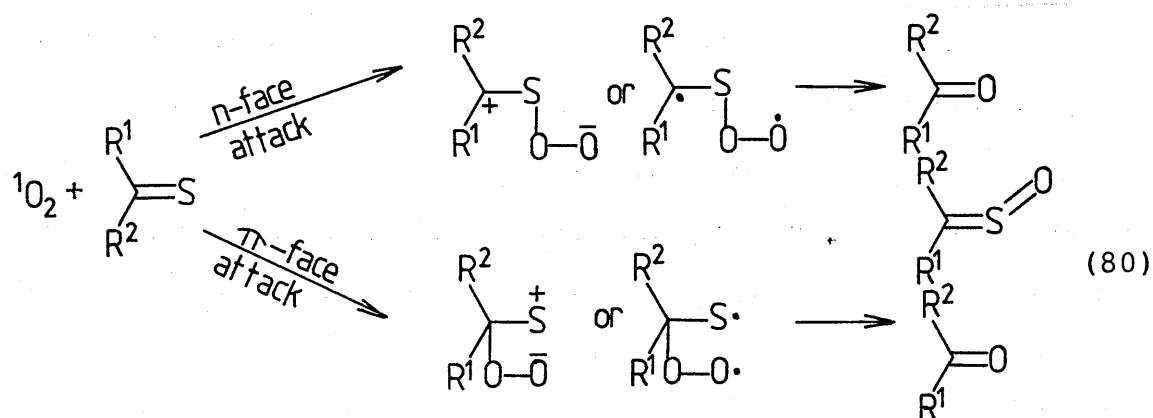


A mechanism which has been proposed to account for these results involves a dipolar acyclic intermediate (78). This intermediate can cyclise to a 1,2,3-dioxathietane, which breaks down to give ketone, or it can eliminate an oxygen atom to give sulphine, either directly or via an oxathiirane¹²⁶. The only available evidence for a dioxathietane intermediate arises from the oxidation of xanthione and related compounds, in which a weak chemiluminescence is seen¹²⁷. This chemiluminescence can be enhanced by added fluorescer and is thought to arise from the decomposition of the dioxathietane (79, X = O).





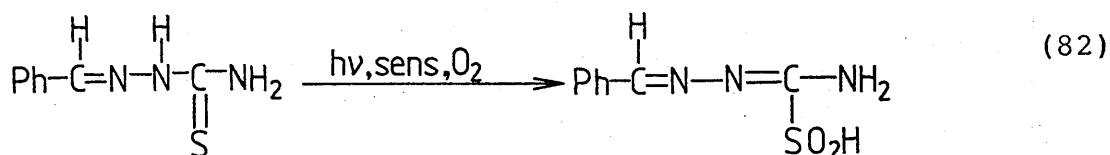
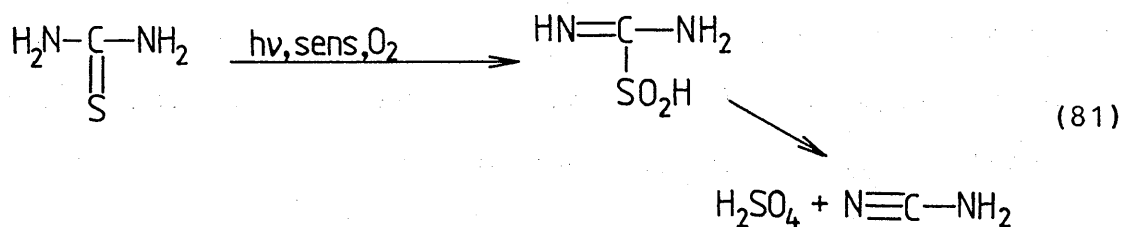
Although only one type of acyclic intermediate has been shown in equation (78), two different types might be possible, depending on whether the singlet oxygen molecule interacts with a π -orbital or with a non-bonding orbital on sulphur (80)¹²⁶. A study of a range of alkyl thioketones showed that the quenching of singlet oxygen correlated with the ionisation energies of the n, rather than the π , electrons¹²⁶. No such comparison could be drawn for aryl thioketones as the ionisation energies were unavailable.



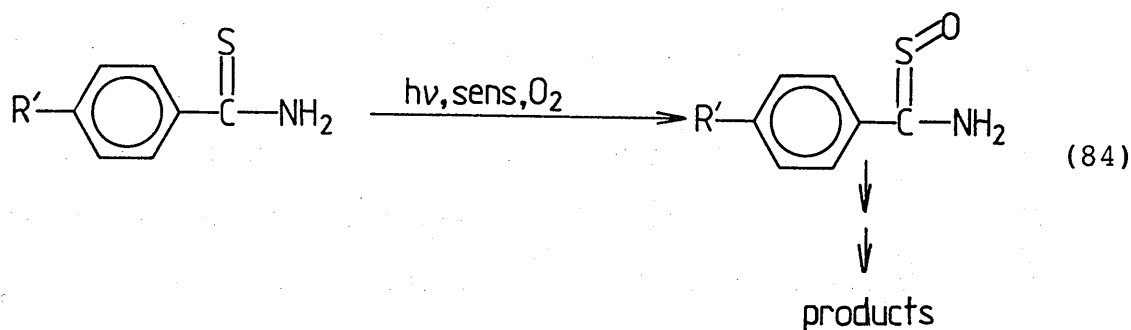
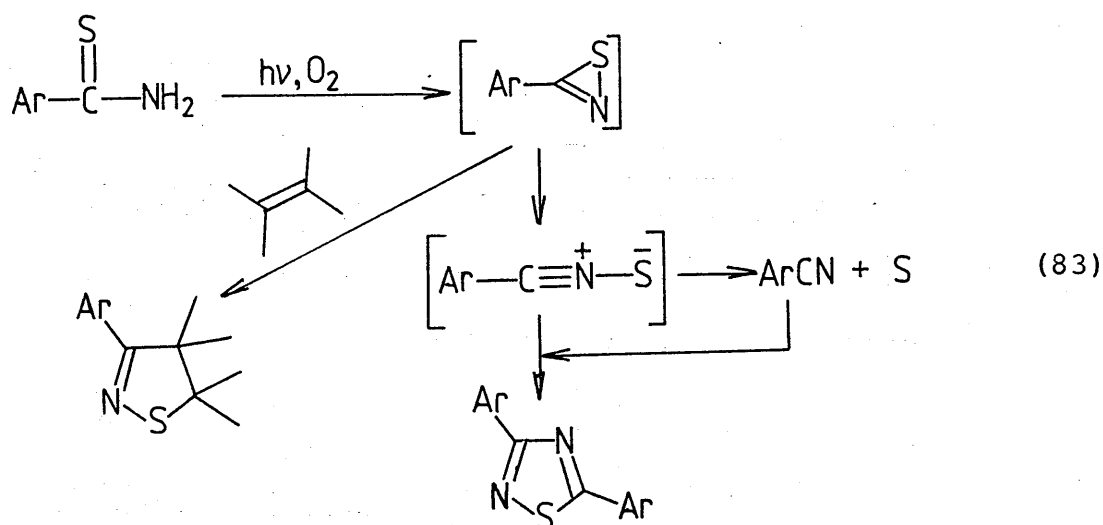
One consideration which has a bearing on the mechanistic schemes is that of singlet oxygen oxidation of sulphines¹²⁸, and it seems that the reaction is subject to steric and electronic effects, but not all sulphines are oxidised.

A range of other thiocarbonyl compounds can be photo-oxidised to give ketones or sulphines, including cyclopropenethione¹¹¹, *O*-alkyl thioesters¹²⁹, 1,2-benzodithiole-3-thione¹³⁰ and α,β -unsaturated thioketones¹³¹.

Thiourea derivatives give different types of products on photo-oxidation. Thiourea itself undergoes chlorophyll-sensitised oxidation to cyanamide and sulphuric acid (81); this process has been used as the basis for an actinometric system¹³². Benzaldehyde thiosemicarbazide is similarly oxidised¹³³, but stops at what is the intermediate stage for thiourea (82), as does 2-imidazolinethione¹³⁴.

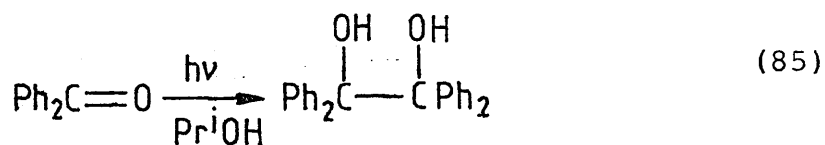


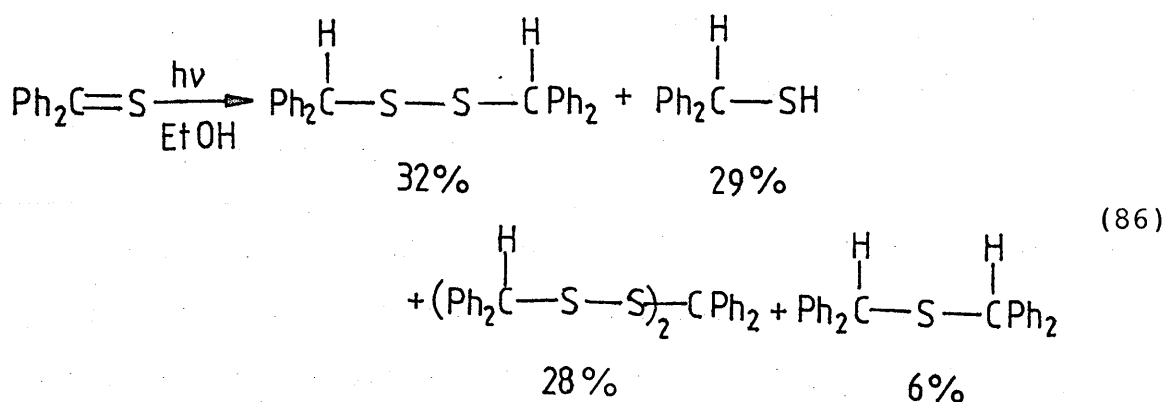
The photo-oxidation of thiobenzamides has been found to give aryl nitrile sulphides¹³⁵ as products (83). A different study has concluded that the first-formed product is a sulphine (84), but full details of the products have not yet been published¹³⁶.



Hydrogen abstraction

Both intermolecular and intramolecular hydrogen abstraction can take place following photochemical excitation; the latter often leads to cyclised products. Intermolecular reaction leading to photoreduction is a process which has been thoroughly investigated for ketones such as benzophenone, which normally gives benzpinacol as the major product (85). However thiobenzophenone gives a wider range of products¹³⁷ (86) with a good hydrogen donor such as a primary alcohol.



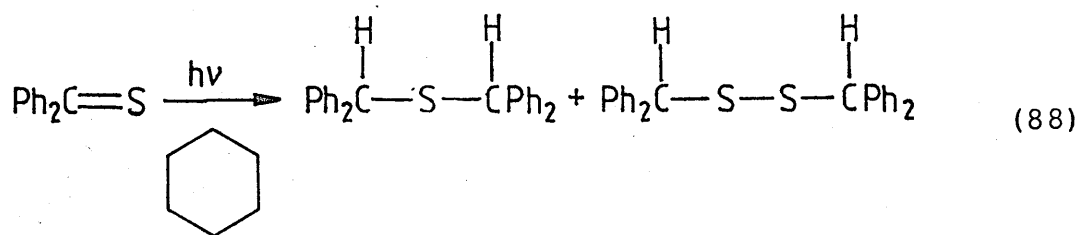


The reaction takes place via the (n,π^*) triplet state of the thione, and deuteration studies have shown that the radical which is formed initially is $\text{Ph}_2\dot{\text{C}}\text{SH}$, and not the alternative $\text{Ph}_2\text{CH}-\dot{\text{S}}$. The radical $\text{Ph}_2\dot{\text{C}}\text{SH}$ is also thought to account for a short-lifetime transient observed by E.S.R.¹³⁸ when thiobenzophenone is irradiated in tetrahydrofuran. The related radical (87) which is formed under the same conditions, has a half-life of 90 seconds and has been characterised by E.S.R.



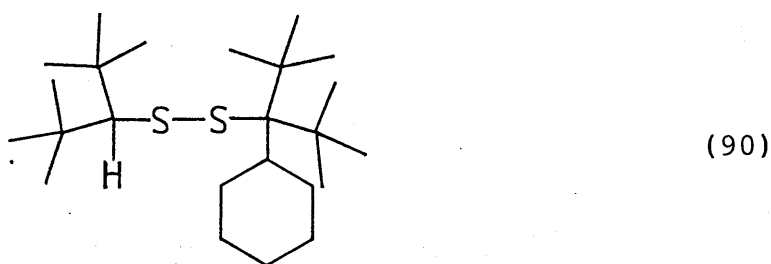
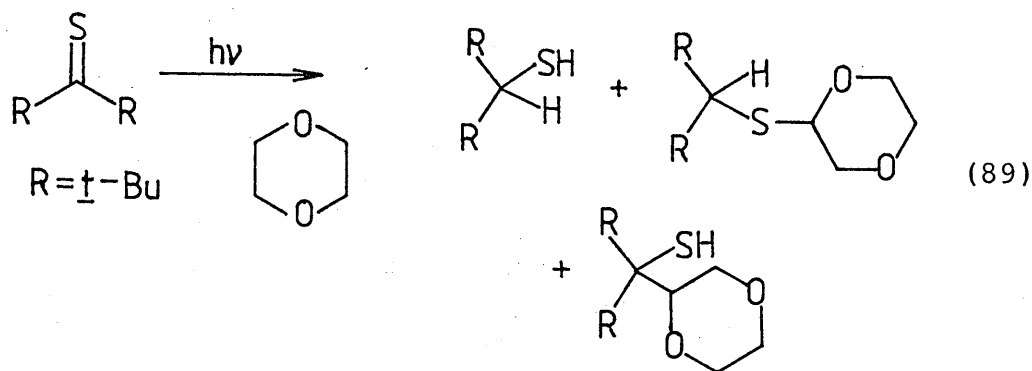
Ground-state thiobenzophenone is a good radical trap; radical (87) may well arise from the trapping of a solvent radical by thiobenzophenone. Some products arise from this interaction; other products are formed because there is an equilibrium between the radicals $\text{Ph}_2\dot{\text{C}}-\text{SH}$ and $\text{Ph}_2\text{CH}-\dot{\text{S}}$, which are not greatly different in energy.

No hydrogen abstraction reaction from $S_1(n,\pi^*)$ or $T_1(n,\pi^*)$ is observed for thiobenzophenone in saturated hydrocarbon solvents. However excitation of thiobenzophenone to $S_2(\pi,\pi^*)$ in cyclohexane leads to the formation of di(benzhydryl) sulphide and di(benzhydryl) disulphide (88)¹³⁷.

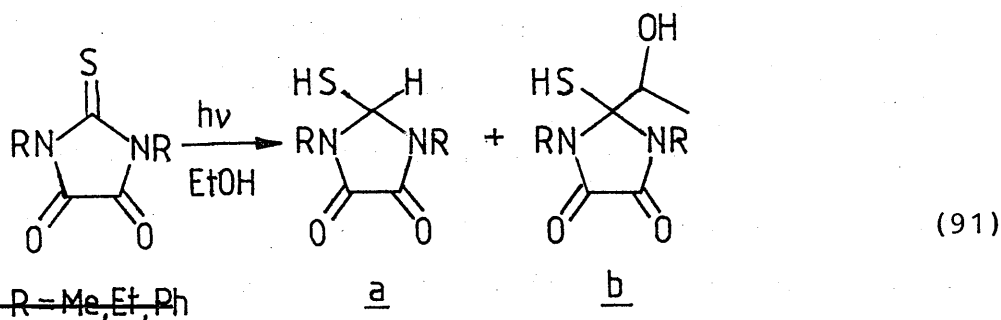


More reactive hydrocarbons, such as cyclohexa-1,4-diene where the overall driving force is the formation of benzene, are subject to hydrogen abstraction by thiobenzophenone following excitation to either the S_1 or S_2 state¹³⁹. The authors have suggested an electron-transfer mechanism, but the evidence is inconclusive. Xanthione is another diaryl thio-ketone which undergoes photochemical hydrogen abstraction¹⁴⁰.

Aliphatic thioketones have been found to behave similarly. Di-t-butyl thioketone can abstract only more labile hydrogen atoms as are found in donors such as amines, toluene or benzyl alcohol, when it has been excited into S_1 or sensitised to give T_1 directly. Some support for the proposed electron-transfer mechanism arises from the lack of reactivity shown by isopropanol or diethyl ether in this reaction and also from the correlations between the reactivity and ionisation potential of aromatic compounds¹⁴¹. However excitation to S_2 allows reaction with a wider range of hydrogen donors¹⁴², leading to the formation of photoadducts in addition to the expected photoreduction products (89). Using cyclohexane as a solvent it was shown that an increase in thioketone concentration correlates with an increased formation of the mixed disulphide product (90) due to radical trapping by the ground state thioketone.

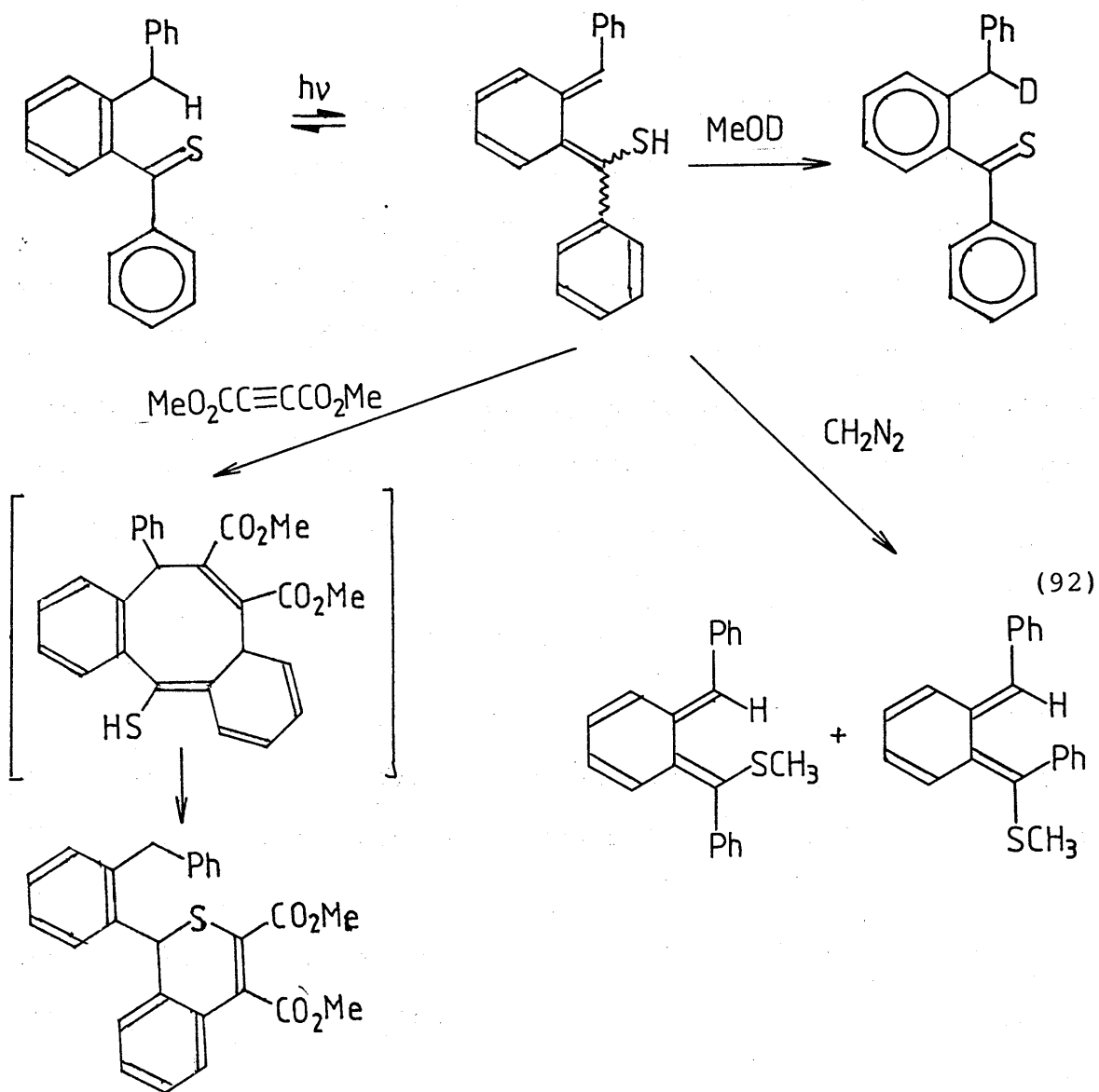


Other thiocarbonyl compounds which have been investigated with respect to hydrogen abstraction are adamantanethione¹⁴³, di-t-butylthioketene¹⁴⁴ and thioparabanates¹⁴⁵. The latter give photoreduction and photoaddition products upon irradiation in ethanol (91); in particular diphenylthioparabanate gives a 98% yield of the thiol (91a).



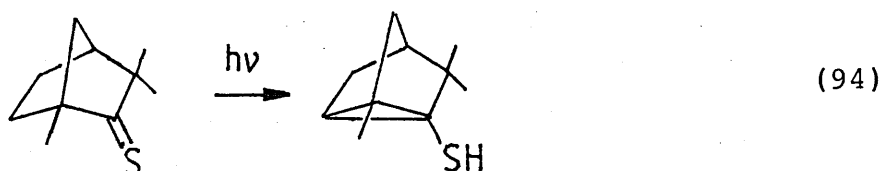
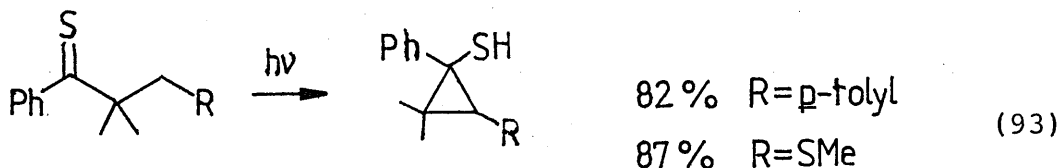
A variety of intramolecular hydrogen abstraction reactions occur for thiocarbonyl compounds. One of the earliest reactions to be investigated was the reversible photoisomerisation of o-benzylthiobenzophenone to give an enethiol (92)¹⁴⁶; this demonstrated that hydrogen abstraction was by the sulphur rather than the thiocarbonyl carbon. The

existence of the enethiol was shown by trapping experiments: in methanol- O-D there is deuterium exchange to give the starting material deuterated at the benzylic position, the addition of diazomethane leads to methylation of the $-\text{SH}$ group, and the addition of dimethyl acetylenedicarboxylate gives rise to a benzothiapyran, which can be accounted for by an initial $(6 + 2)$ cycloaddition to the enethiol.



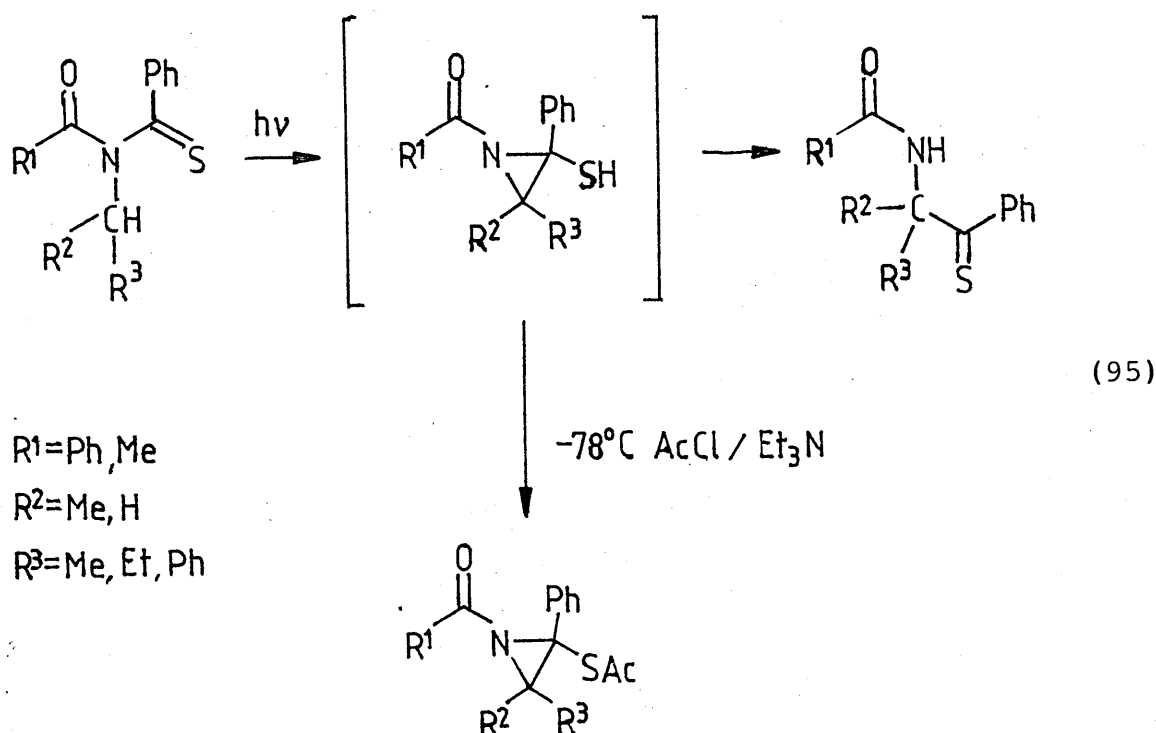
However most of the intramolecular hydrogen abstraction reactions which have been studied are those which lead to cyclised products. The ring sizes in the products range from three to six, as hydrogen abstraction can take place from the β , γ , δ or ϵ positions.

β -Abstraction occurs in thiocarbonyl compounds with structural constraints: cyclopropanethiols are the resulting products from 1,3-diarylpropane-1-thiones (93; R = Ar)¹⁴⁷ or from thiofenchone (94)¹⁴⁸.

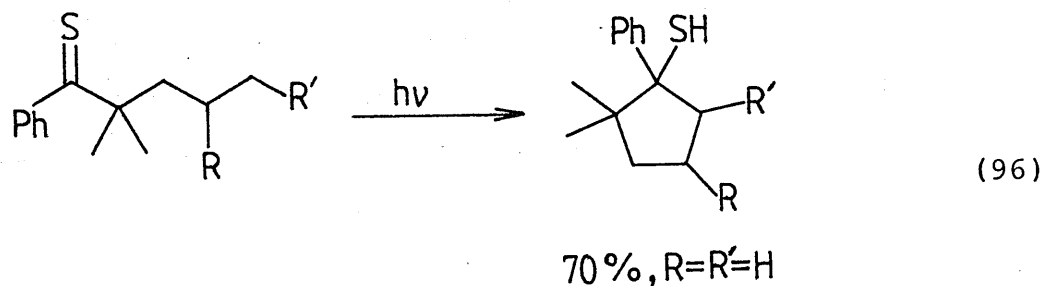


For the 1,3-diarylpropane-1-thiones the cyclopropanethiols are formed by different routes following excitation into either S_1 or S_2 , although a biradical is an intermediate in both cases. As the proportions of stereoisomers which result from the two excitations are not identical, it may be that the lifetime of the triplet biradical (following excitation to S_1) is sufficiently long to allow bond rotation. Thiofenchone reacts from the S_2 state; no triplet reaction was detected. β -Hydrogen abstraction is favoured over the δ -hydrogen abstraction, which could in principle also occur, in certain 2-methylthio derivatives (93, R = SMe)¹⁴⁷; this may be because the β -hydrogen is more labile. As for the other reactions of this type the quantum yield for the disappearance of the 1,3-diarylpropane-1-thione is greater for the S_2 reaction (2.6×10^{-2}) than for the T_1 reaction (5.8×10^{-4}).

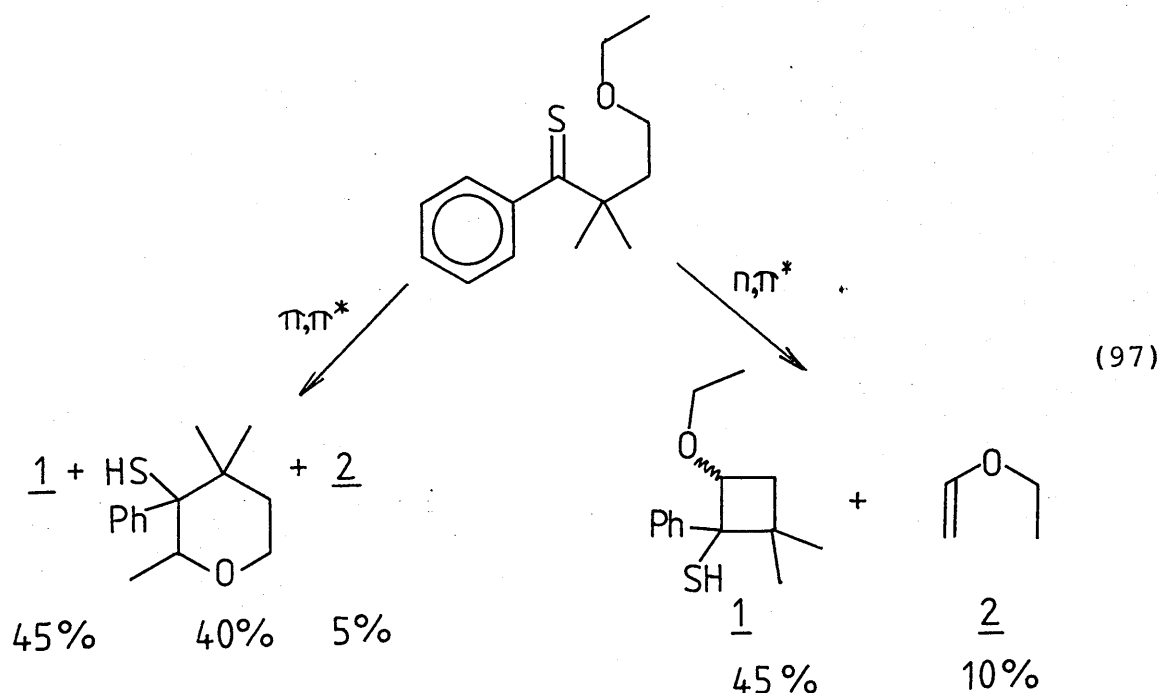
The rearrangement of acyclic N-alkylthioimides upon irradiation may be accounted for in terms of an intermediate cyclopropanethiol, which would be formed following an initial β -hydrogen abstraction (95)¹⁴⁹. The cyclopropanethiol can be trapped by added acetyl chloride.

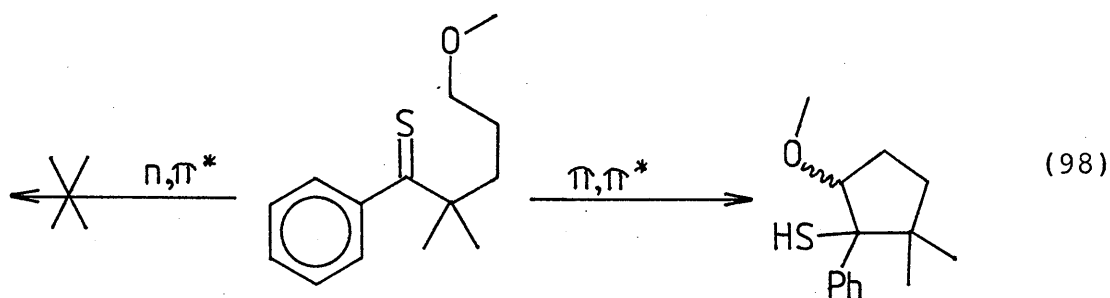


An interesting and useful study of the preference for different sites of hydrogen abstraction was carried out for the aryl alkyl thioketones¹⁵⁰. Following excitation to the S_2 state the preference was for δ -hydrogen abstraction, and thus the formation of cyclopentanethiol product (96). Mechanistic studies showed that reaction occurred from the S_2 state, and that an intermediate biradical was formed. However this biradical may have undergone disproportionation rather than cyclisation, and hence the quantum yield of the reaction was low ($\phi = 0.032$ for $R = \text{Me}$, $R' = \text{H}$). The rate constants and activation energies of these reactions were also determined¹⁵¹.

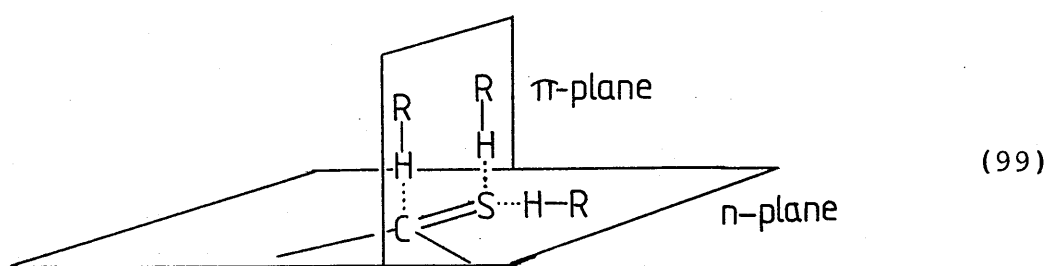


The effect of an oxygen atom in the alkyl chain of aryl alkyl thioketones was also studied¹⁵²; different results were obtained, depending upon the position of the oxygen atom and the reacting state. If there was an oxygen atom at the δ -position, reaction from S_2 gave products following hydrogen abstraction at either the γ - or ϵ -positions, (97), whereas reaction from T_1 gave only γ -hydrogen abstraction products, including a Norrish type II elimination product which was minor for the S_2 reaction. Results from solvent studies, product quenching experiments and fluorescence quenching experiments all served to show that a thione-ether charge-transfer intermediate contributed little to the cyclisation. Another comparison between short and long-wavelength reactions was made for a thione with the oxygen atom at the ϵ -position: the latter gave no product after several days irradiation at $\lambda > 445$ nm whereas the former gave a δ -hydrogen abstraction product in high yield (98) following eight hours irradiation with a medium-pressure mercury arc and a Pyrex filter.

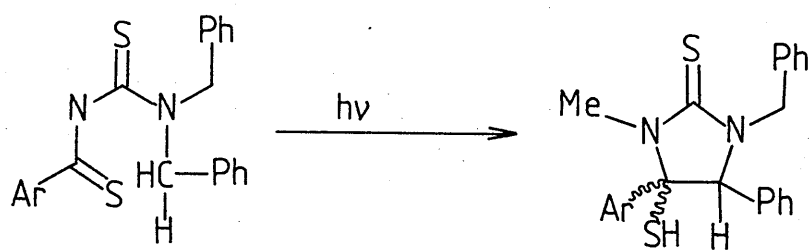




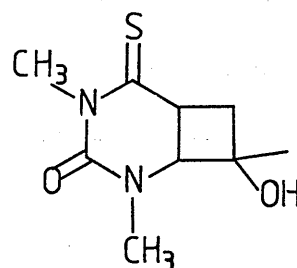
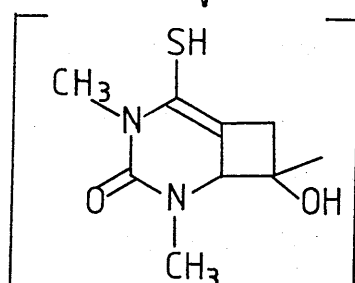
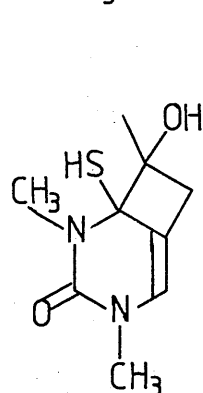
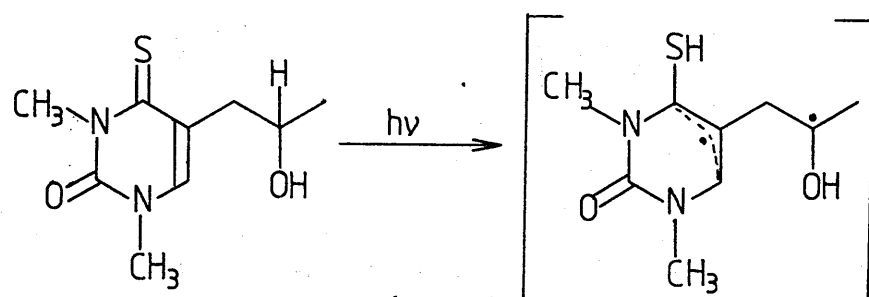
A theoretical study on thioketone hydrogen abstraction reactions¹⁵³ takes into account the energies of the excited states and direction of approach of the hydrogen donor atom. The differences in geometry are explained in that for n approach, in which the atoms S-H-C are coplanar in the n plane, the (n, π^*) states are geometrically more favourable while for π approach the (π, π^*) (i.e. hydrogen capture by sulphur or carbon) states are geometrically more favourable (99). The lack of reactivity shown by the (n, π^*) states towards hydrogen abstraction is due to the energies of these states, which are too low for hydrogen abstraction except for particularly labile hydrogen atoms, although these states are actually more geometrically accessible than the (π, π^*) state.



N-Thioaroylthioureas show δ -hydrogen abstraction to give imidazolidinethiones (100)¹⁵⁴. It is not known which excited state is responsible for this reaction, but it is noted that only a strongly-activated hydrogen can be abstracted. This is also the case for the 5-substituted 4-thiouracils (101)¹⁵⁵. In these compounds there is an alternative closure position for the intermediate biradical due to allylic resonance.



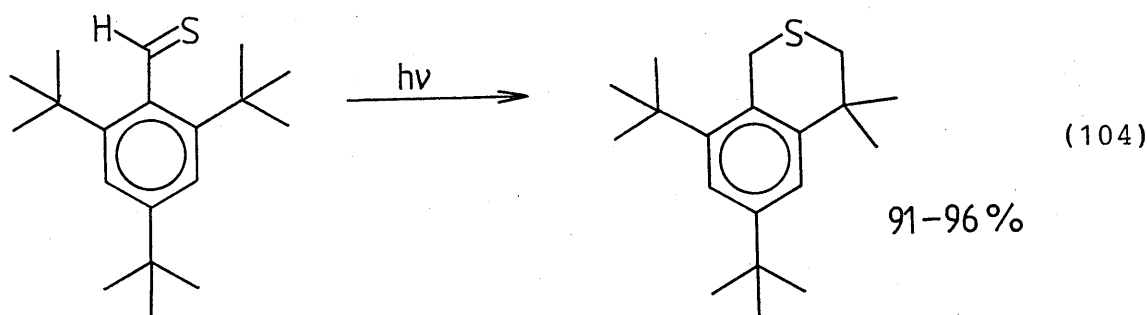
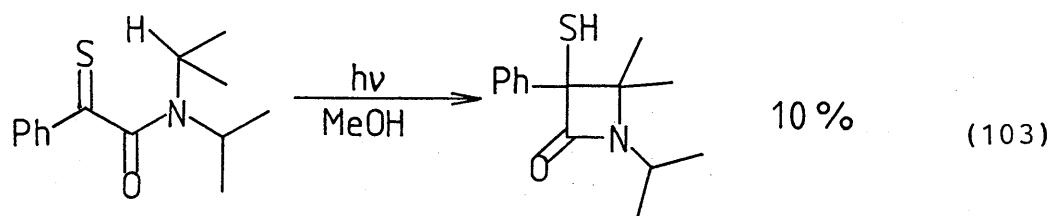
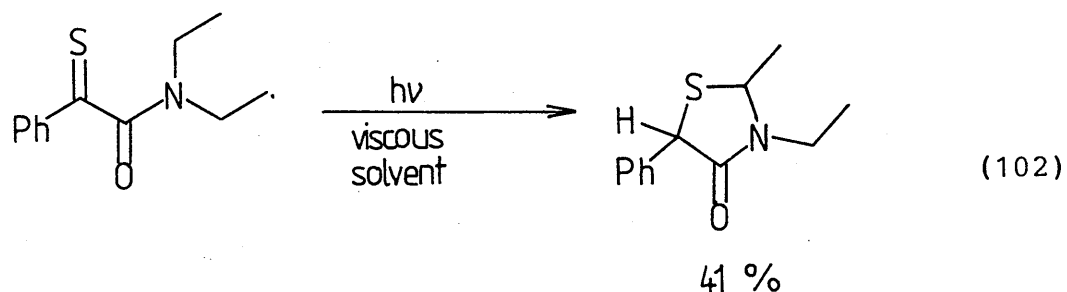
(100)



(101)

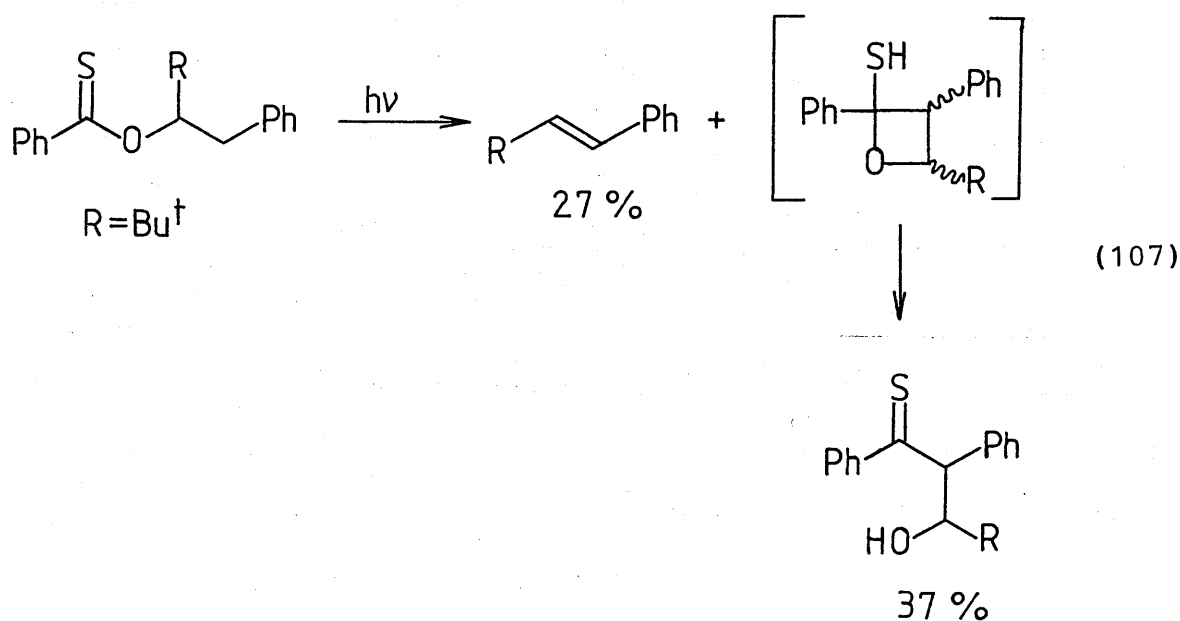
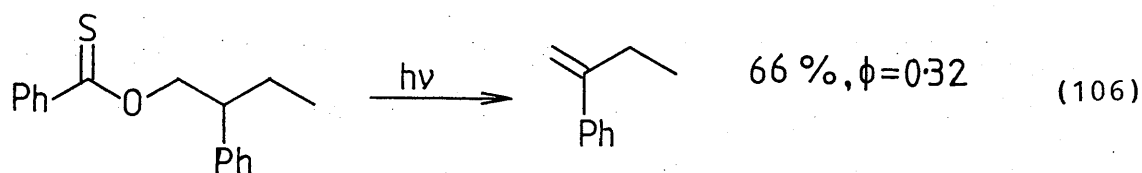
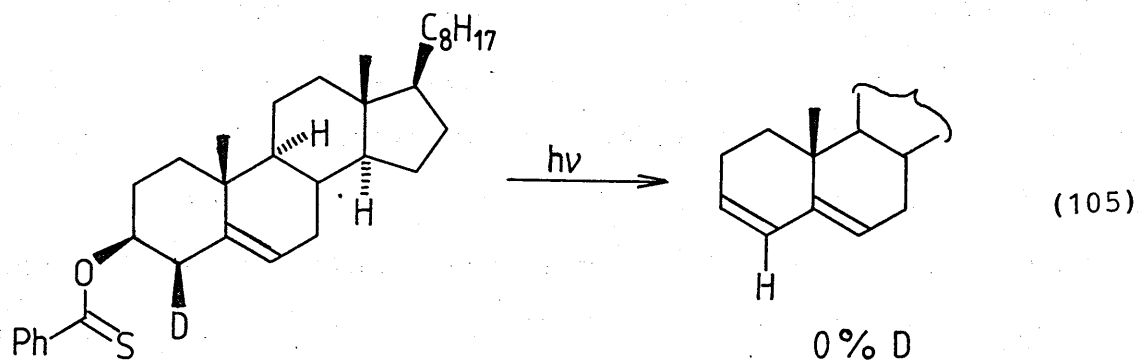
There are some compounds in which the overall hydrogen transfer is to the carbon, rather than to the sulphur, of the thiocarbonyl group. Some N,N-dialkyl- α -thioxoamides lead to

thiazolidinone products (102) following γ -hydrogen abstraction, whereas others give the β -lactam which might be expected on the basis of previous results (103)¹⁵⁶. These reactions are thought to proceed from the S_2 state and involve an electron-transfer mechanism. The photocyclisation of 2,4,6-tri-*t*-butylthiobenzaldehyde also shows a product from overall δ -hydrogen abstraction by the carbon (104)¹⁵⁷; this is an interesting reaction in view of the fact that it seems to proceed equally easily following excitation to either S_1 or S_2 .

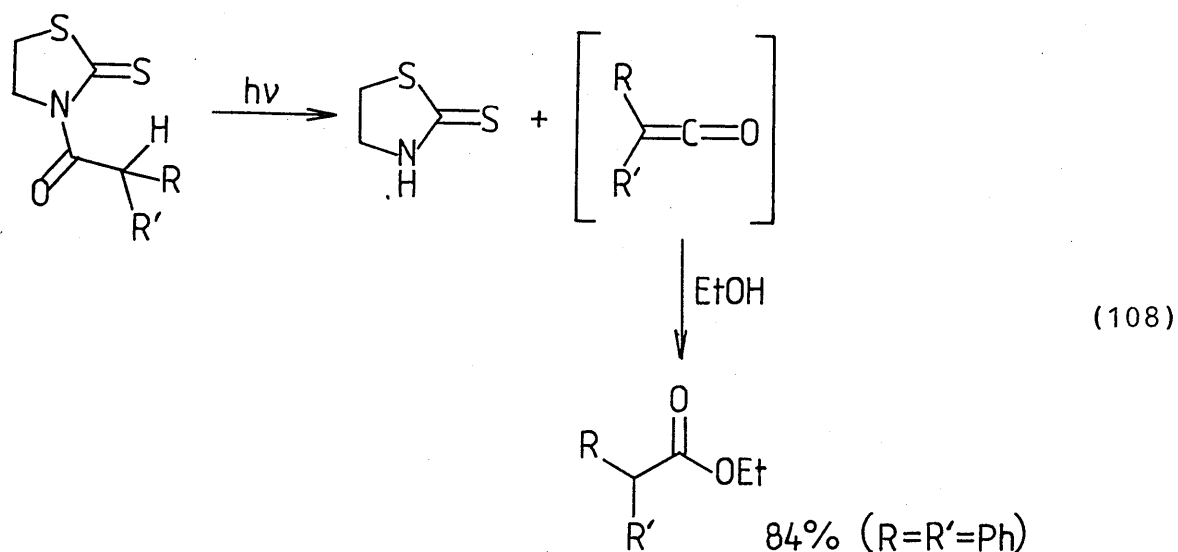


O-Alkyl thiobenzoates can undergo a Norrish type II photoelimination; this is a useful, mild method for the dehydration of homoallylic alcohols¹⁵⁸. A wide variety of compounds can be treated in this way, including cholesterol (105)¹⁵⁹. The reaction is stereospecific, and the quantum

yields are fairly high (106)¹⁶⁰. The mechanism is via the (n, π^*) triplet state and a 1,4-biradical: it has been shown that the biradical does not revert to the starting material by studying an optically active O-alkyl thiobenzoate. There is a competing reaction for the biradical, which is comparatively fast for some substituent patterns, leading to a β -hydroxy-thioketone via a ring-closed oxetane-2-thiol (107)^{93,161}.



This reaction is not seen for alkyl dithiobenzoates or for N-substituted thiobenzamides: the lack of reactivity has been attributed⁹³ to either a low (n, π^*) energy, or to the lowest triplet state being (π, π^*). However N-acyl-2-thioxo-thiazolidines undergo a γ -hydrogen abstraction, to give 2-thioxothiazolidine as a Norrish type II elimination product (108)¹⁶².

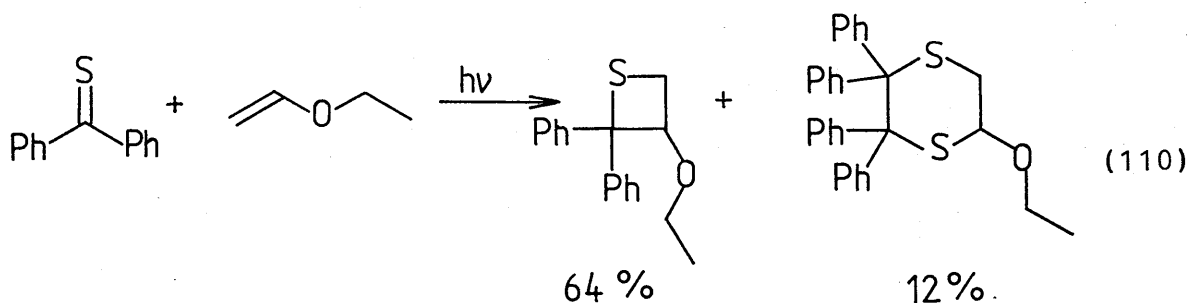
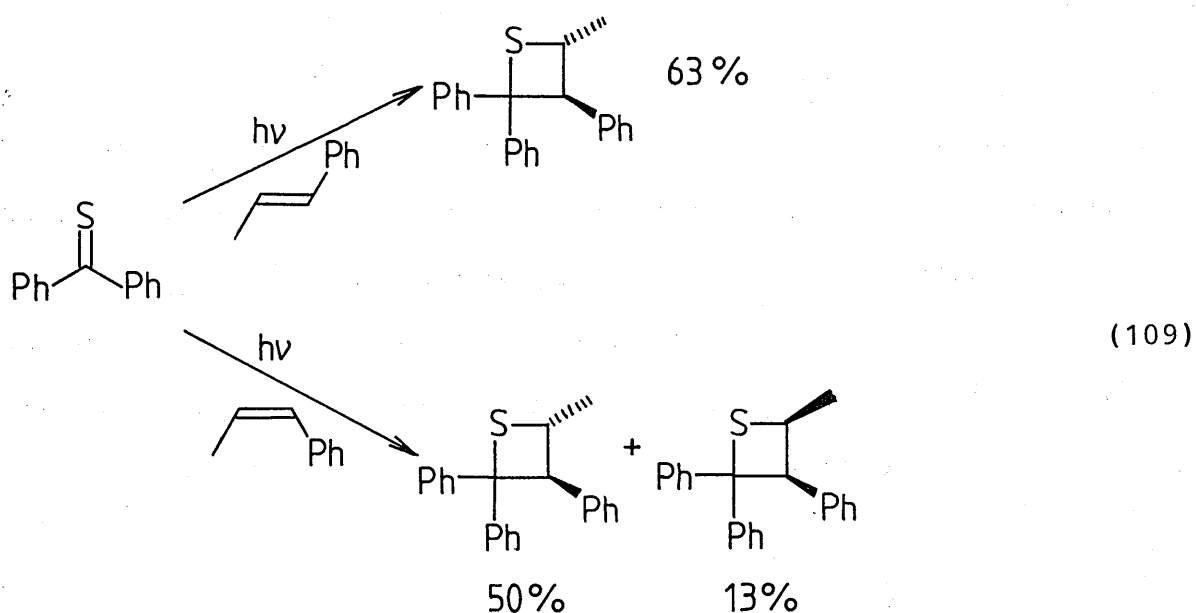


Photocycloaddition reactions

The area of thiocarbonyl photochemistry which has been most widely studied and reviewed⁶⁹ is photocycloaddition; such reactions take place not only with alkenes but also with other carbon-carbon and carbon-heteroatom multiple bond systems. These reactions are influenced by the substituents around the thiocarbonyl group, the substituents around the multiple bond, and most importantly, they are wavelength dependent.

The T_1 reaction of thiobenzophenone (and of other aromatic thiones) with a variety of electron-rich alkenes, such as alkyl aryl, alkoxy or alkylthio alkenes, leads to thietanes and/or 1,4-dithianes as products. Reactions with cis- or trans-1-phenylpropene show regioselectivity, but not stereoselectivity (109)¹⁶³: the rotation about the carbon-carbon

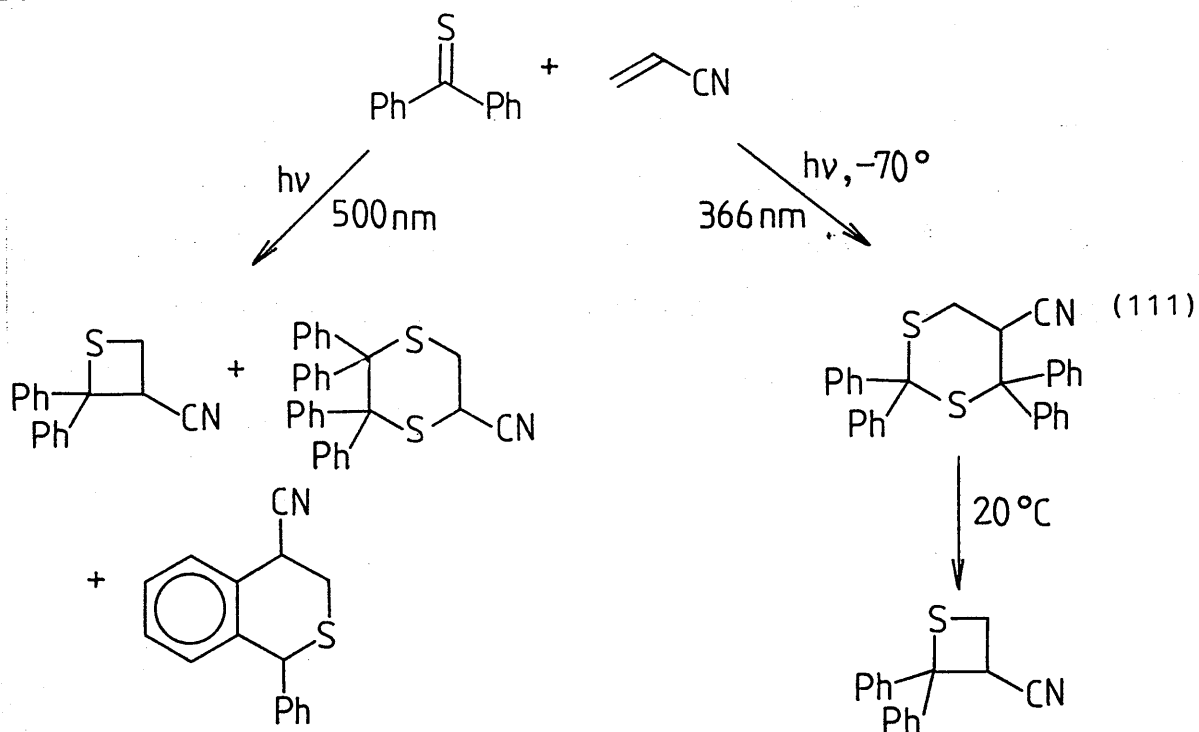
bond (derived from the alkene C=C) in the biradical intermediate must therefore be faster than ring-closure. Reaction with ethyl vinyl ether leads to one orientation of thietane, together with a dithiane product (110)¹⁶⁴. The formation of the dithiane arises from the trapping of a biradical intermediate by a molecule of ground-state thioketone. This product is dependent upon the steric bulk of the alkene - bulkier alkenes (e.g. styrene) tend to favour dithiane formation¹⁶⁵ - and also upon the concentration of the ground-state thioketone present.



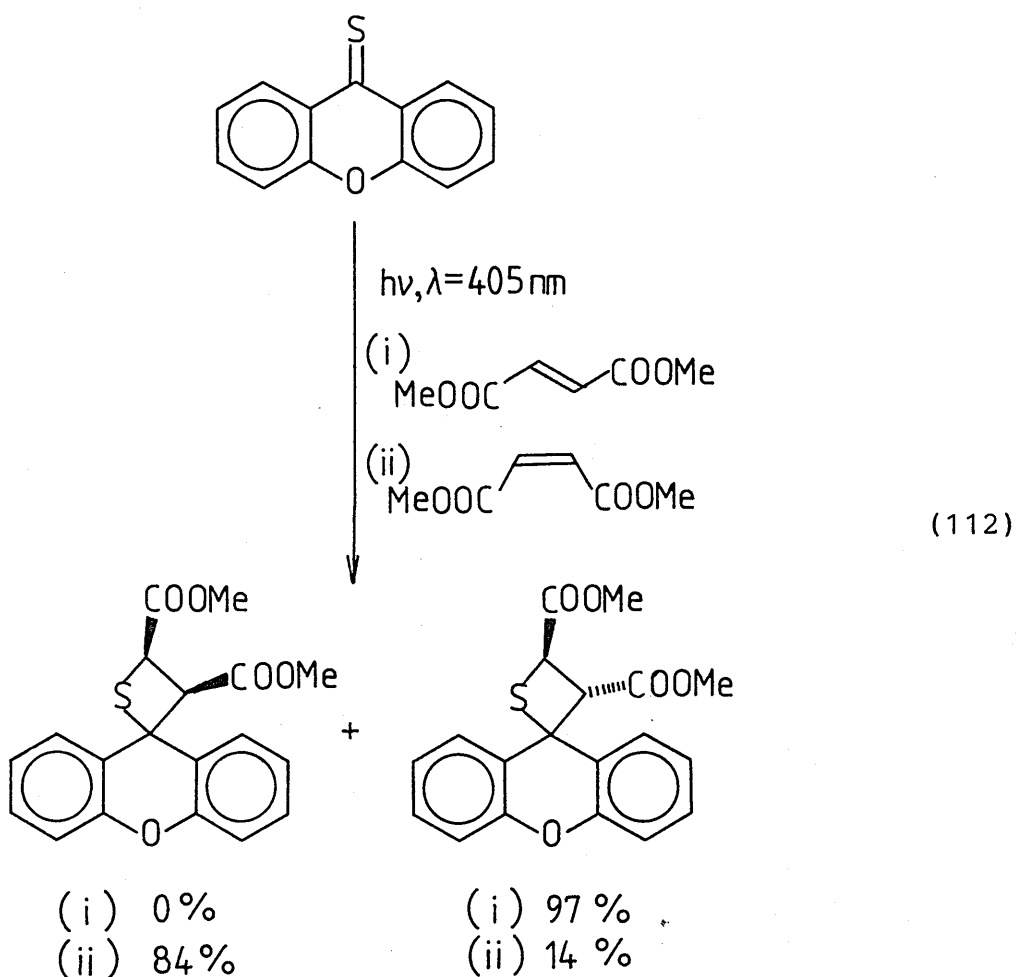
Further support for the biradical intermediate comes from the observed cis-trans isomerisation of the recovered alkene¹⁶⁶, and the relative rates of attack of thiobenzophenone on a series of alkenes¹⁶⁷. Electron-rich alkenes which react with

thiobenzophenone are cyclohexene, butyl vinyl sulphide¹⁶⁵ and acenaphthylene¹⁶⁸. Xanthione behaves similarly^{169,170}.

Reaction of triplet thiobenzophenone with electron-poor alkenes is so inefficient that it was originally thought not to take place at all¹⁷¹; further investigation revealed a reaction of low efficiency with alkenes such as acrylonitrile¹⁷² or methyl acrylate¹⁷³, yielding a thietane, a 1,4-dithiane and a benzothiapyran which is derived via attack on one phenyl ring in the intermediate (111). However reaction with acrylonitrile following excitation to S_2 leads to the thietane as the major product (93%); this thietane is thought to be formed following reaction from S_2 ⁹¹, which gives a 1,3-dithiane as an intermediate (111)¹⁷⁴. The intermediate 1,3-dithiane was isolated from a low temperature irradiation: ultraviolet and ^1H -NMR spectral data together with microanalytical data were used to establish the structure. On warming, the 1,3-dithiane decomposed to form thiobenzophenone and the thietane as sole products. This S_2 reaction is more efficient than the T_1 reaction.

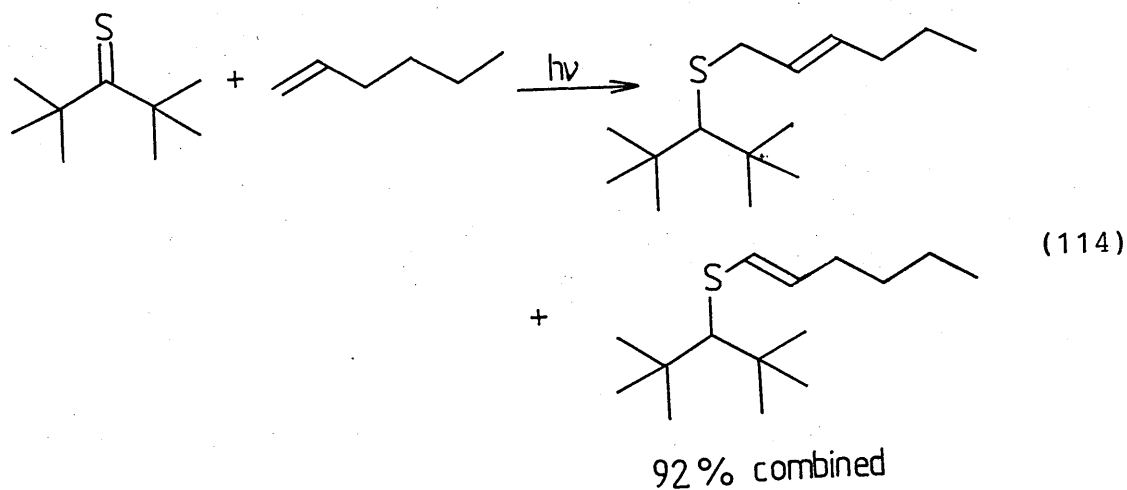
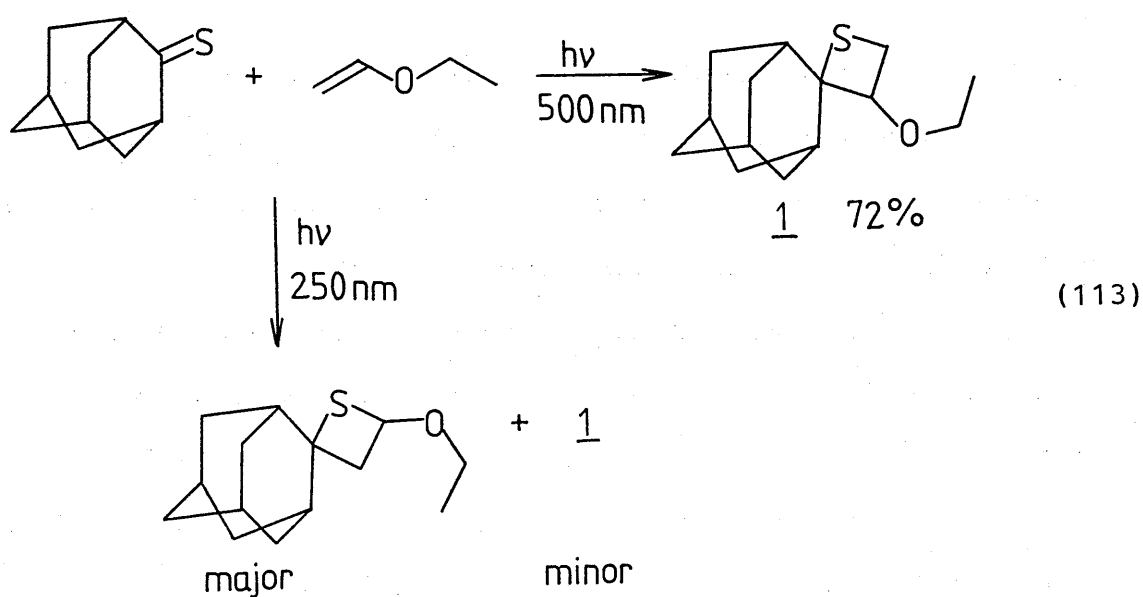


The stereoselectivity of the S_2 photocycloaddition is demonstrated in the reaction of thiobenzophenone with cis- or trans-1,2-dichloroethene¹⁶⁷, or that of xanthione with dimethyl fumarate or maleate¹⁷⁵. On irradiation with light of 405-408 nm, xanthione reacts with dimethyl maleate to give mainly the cis-thietane; with dimethyl fumarate the product is mainly the trans-thietane (112). By contrast, irradiation of xanthione at 589 nm gives trans-thietane from both alkenes.

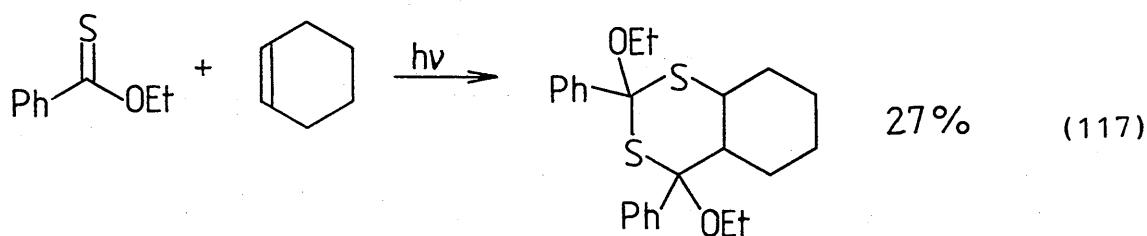
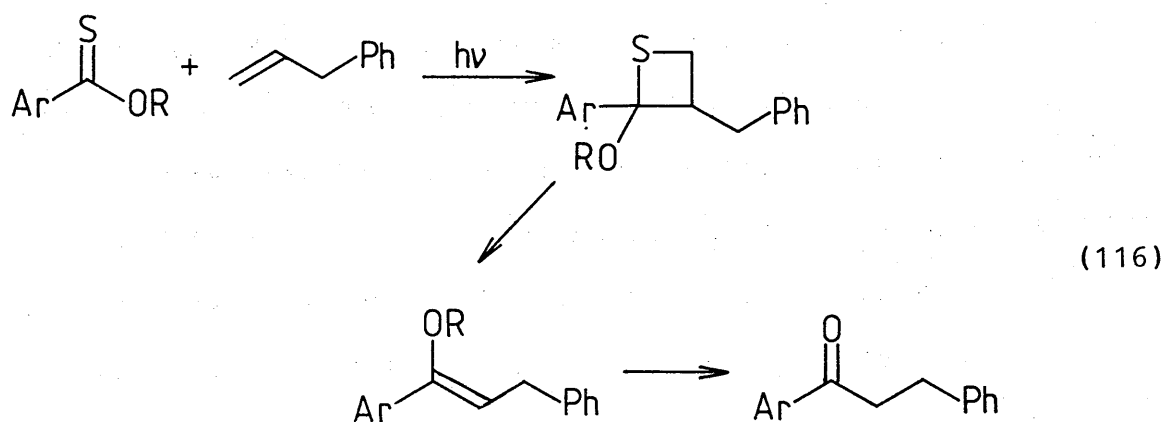
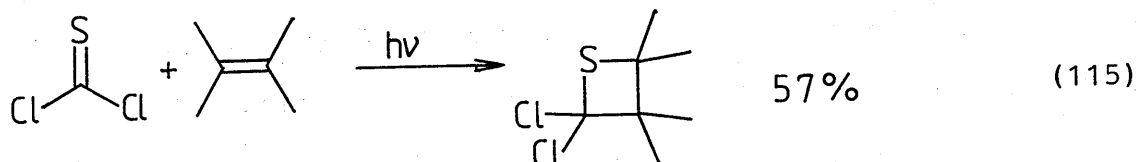


Aliphatic thioketones behave similarly to the aromatic compounds. The long-wavelength irradiation of adamantanethione with ethyl vinyl ether gives a thietane at low efficiency ($\phi = 0.0009$); by comparison the short-wavelength irradiation is a more efficient process ($\phi = 0.019$) in which the other regioisomer is also formed (113)⁷⁸. Photocycloaddition

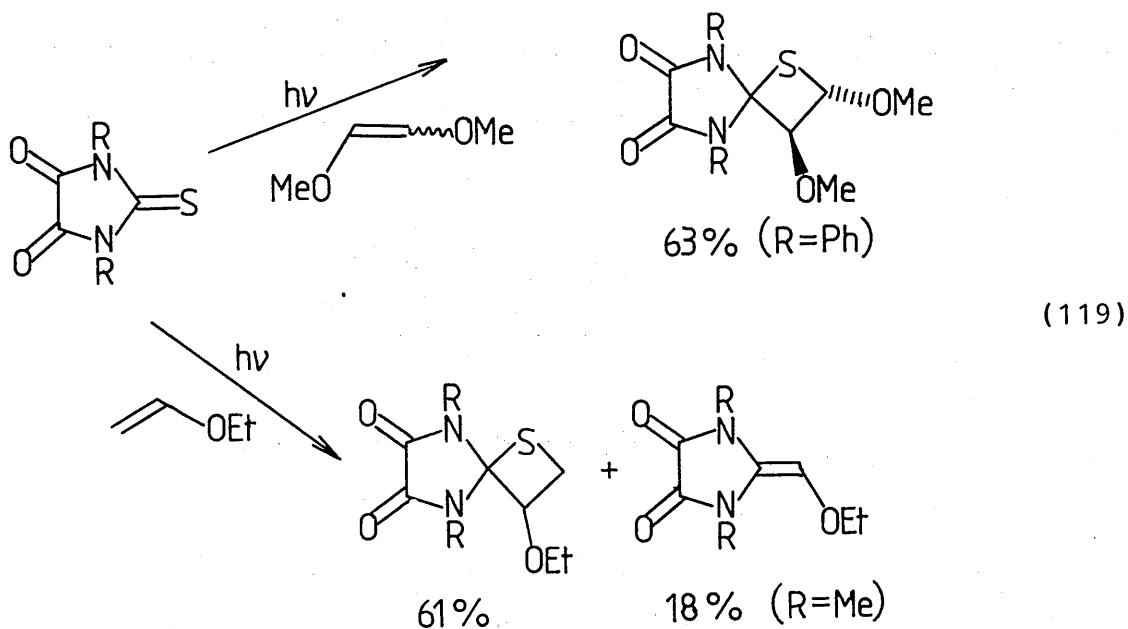
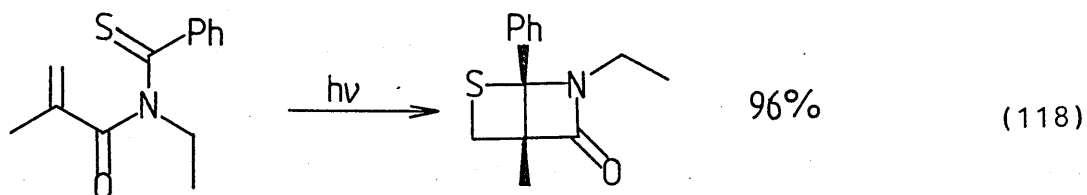
reactions with acrylonitrile, fumaronitrile and maleonitrile show that the T_1 reaction is regioselective but not stereoselective, and that S_2 reaction is stereoselective but not regioselective. Di-t-butyl thioketone shows no photocycloaddition reactions from T_1 , but from S_2 the reactions are stereoselective and non-regioselective¹⁷⁶. Alkenes such as hex-1-ene lead to acyclic products, probably via hydrogen abstraction in a biradical intermediate¹⁷⁷. It seems likely that steric hindrance inhibits ring-closure to a thietane (114).



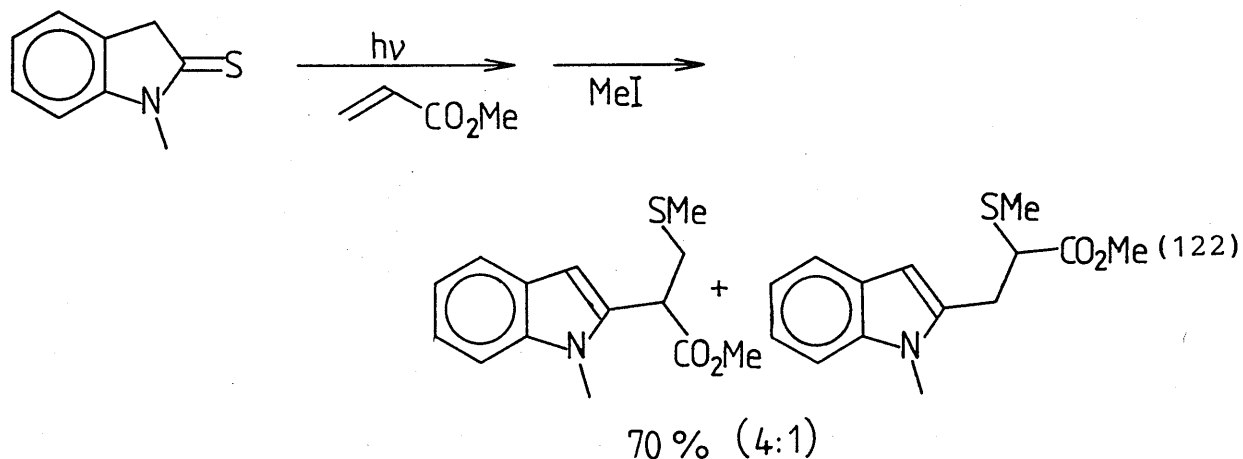
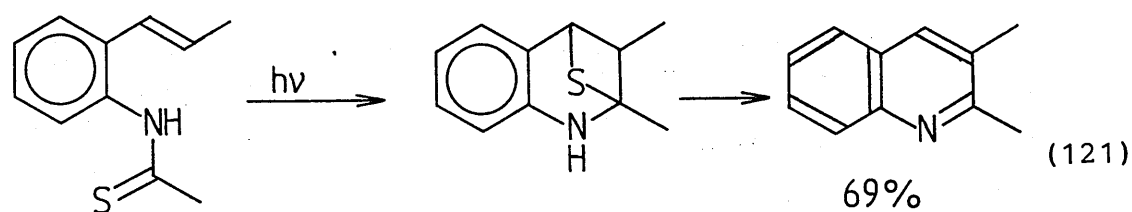
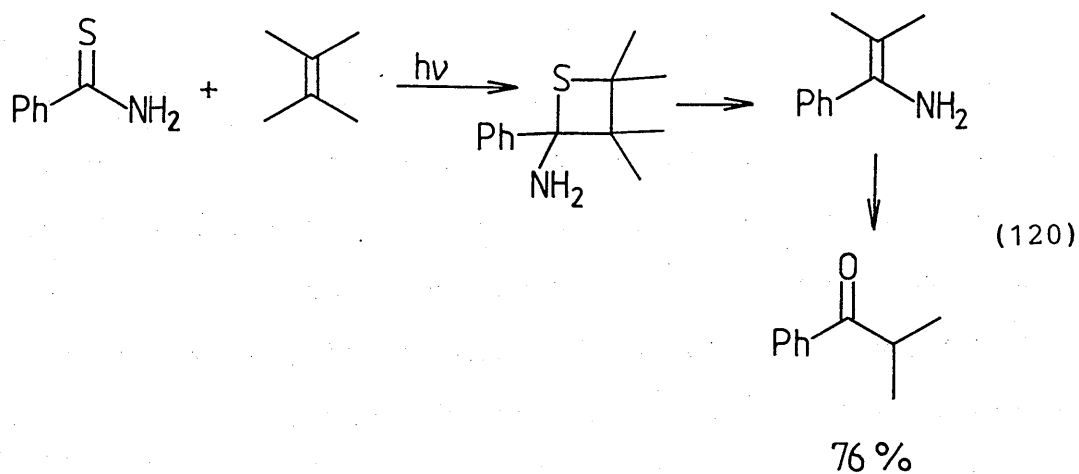
Other types of thiocarbonyl compounds will also undergo photocycloaddition to alkenes. Thiophosgene (115)¹⁷⁸, di-O-phenyl thiocarbonate¹⁷⁹ and O-alkyl thioesters¹⁷² give reasonable yields of thietanes, although these often undergo sensitised cleavage to the corresponding enol ether and hence a ketone product after work-up (116)¹⁸⁰. The O-alkyl thioesters may also yield 2,4-dialkoxy-1,3-dithianes (117).



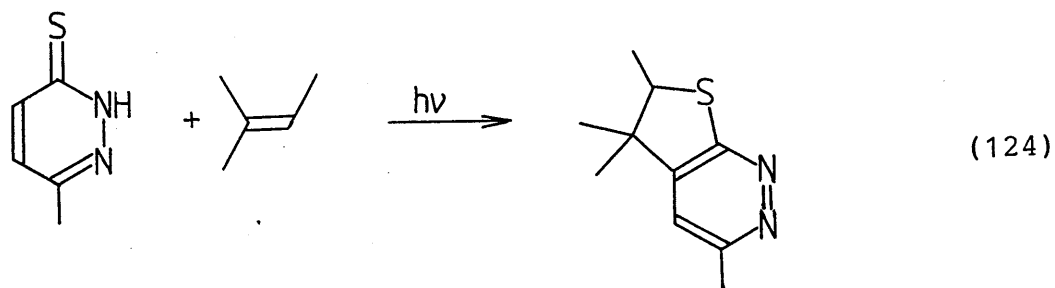
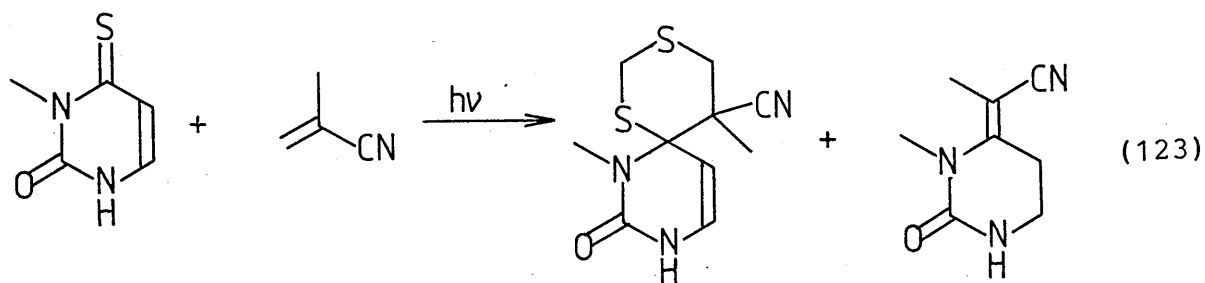
The intramolecular photocycloaddition of an acyclic thioimide with an alkene has been found to lead to fused β -lactams (118)¹⁸¹. Thioparabanates undergo photocycloaddition reactions in an intermolecular manner with alkenes, yielding spirothietanes or an elimination product which is derived from a spirothietane (119)¹⁸².



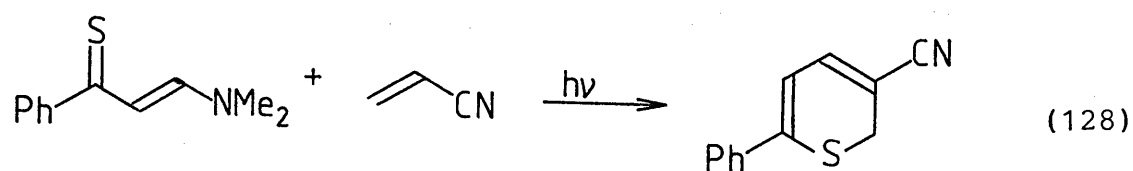
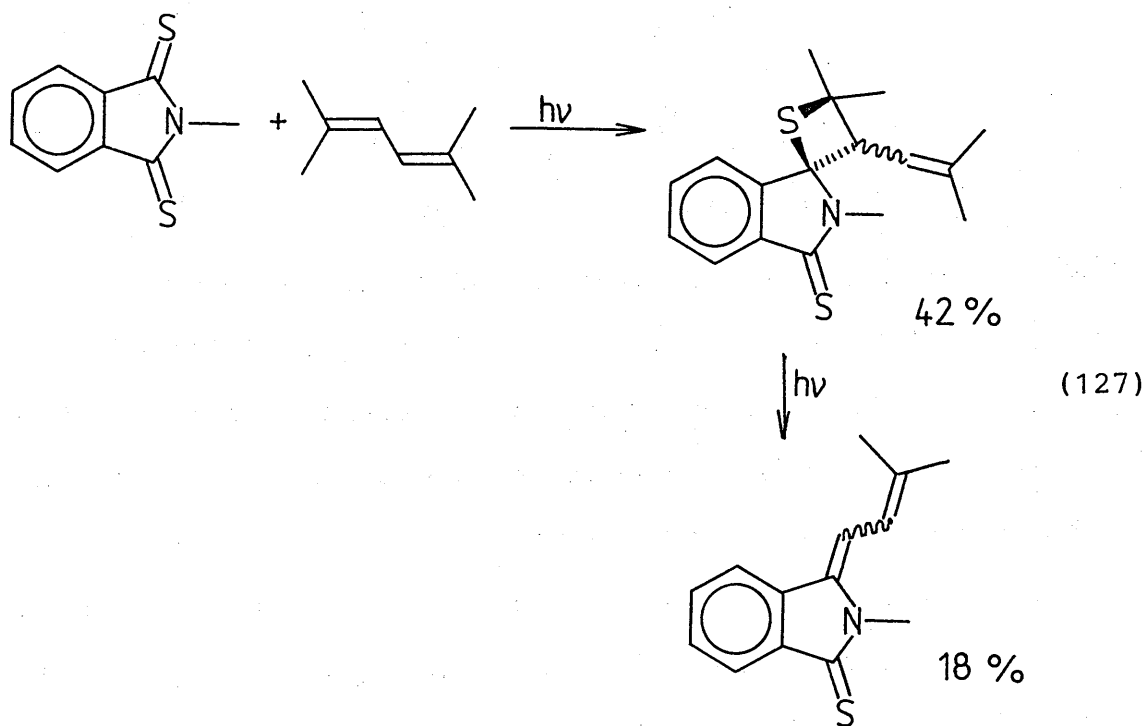
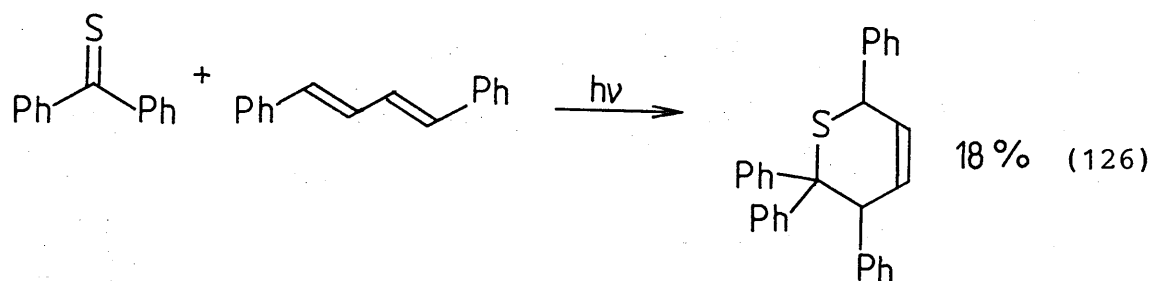
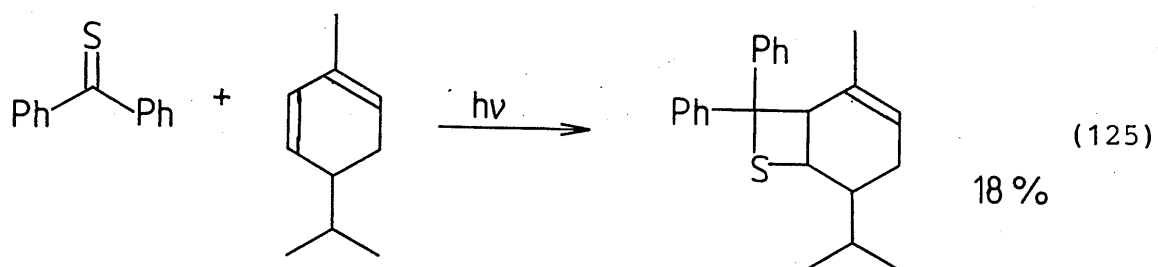
The photoreactions of thioamides with alkenes do not lead to isolable thietane products, although it seems likely that these may be intermediates. The reaction of thiobenzamides with 2,3-dimethylbut-2-ene gives isobutyrophenones, which probably arise via the hydrolysis of the cleavage product of a 2-aminothietane (120)¹³⁵. The intramolecular photocycloaddition of *N*-(*o*-vinylphenyl)thioamides leads to quinolines (121)¹⁸³. The non-regiospecific photocycloaddition of indoline-2-thiones with methyl acrylate, followed by *in situ* methylation, gives a mixture of isomeric substituted indoles (122)¹⁸⁴.



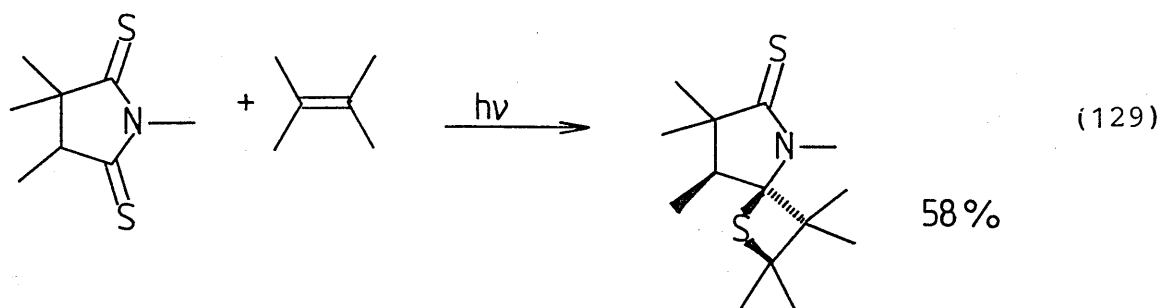
Some reactions of nitrogen-containing thiocarbonyl compounds lead to slightly unusual products. Thiouracils generally yield thietanes in a normal photocycloaddition reaction with alkenes¹⁸⁵, but with methylacrylonitrile the thietane is thought to break down to give the fused 1,3-dithiane and (1-cyanoethylidene) products which are observed (123)¹⁸⁶. Irradiation of a 2,3-dihydropyridazine-3-thione with 2-methylbut-2-ene gives a thieno fused product; note that this includes overall oxidation (124)¹⁸⁷.

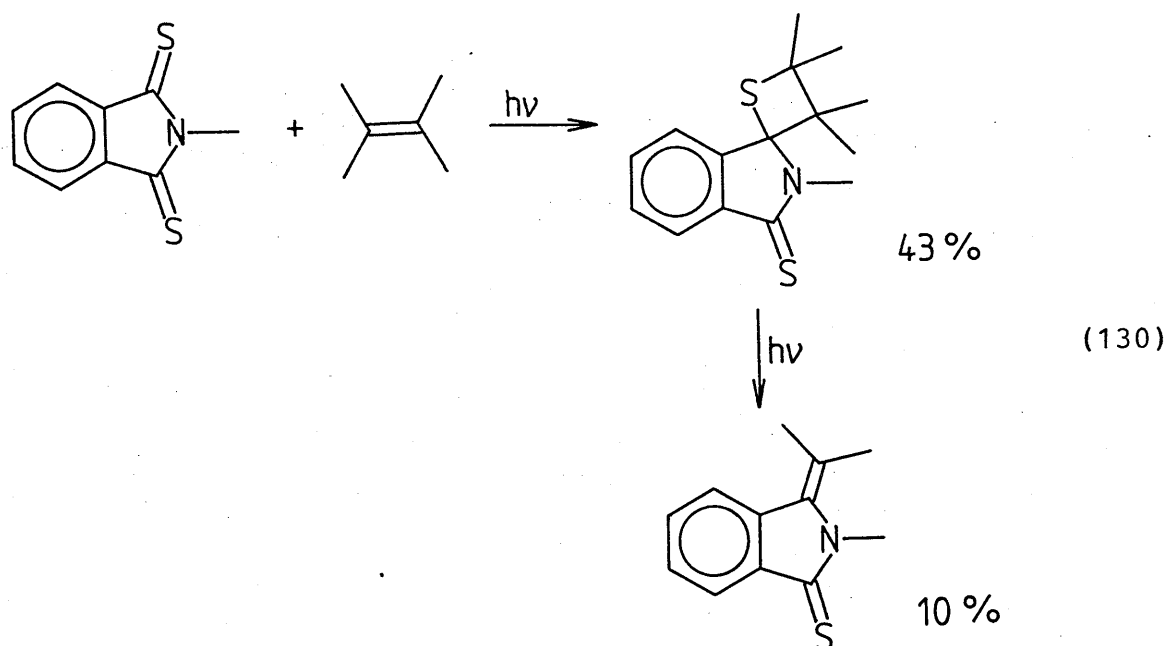


The photocycloaddition reactions of thiocarbonyl compounds with conjugated dienes can lead to (2+2) or (2+4) cycloadducts. Sterically hindered dienes lead to the (2+2) thietanes, e.g. from thiobenzophenone with cycloocta-1,3-diene¹⁸⁸ or with α -phellandrene (125)¹⁸⁹. With less hindered dienes such as cyclopentadiene¹⁸⁸, cyclooctatetraene¹⁶⁸, isoprene or 1,4-diphenylbuta-1,3-diene (126) dihydrothiapyrans are formed. These (4+2) cycloadducts may also be formed thermally¹⁹⁰, but the photochemical reaction is faster. The photocycloaddition of 2,5-dimethylhexa-2,4-diene to N-methyldithiophthalimide gives a (2+2) adduct in the photochemical reaction (127)¹¹⁰ whereas thermal reactions of this thioimide with 1,3-dienes lead to (4+2) adducts¹⁹¹. By contrast the photochemical Diels-Alder reaction of a thiobenzoylenamine shows the conjugated thiocarbonyl group acting as the diene (128)¹⁹².

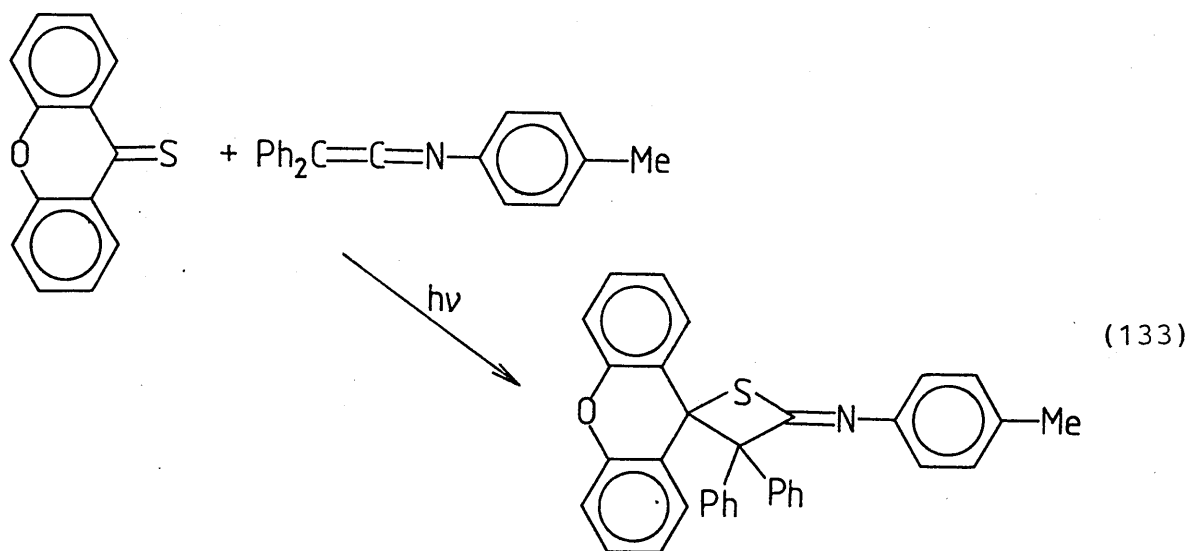
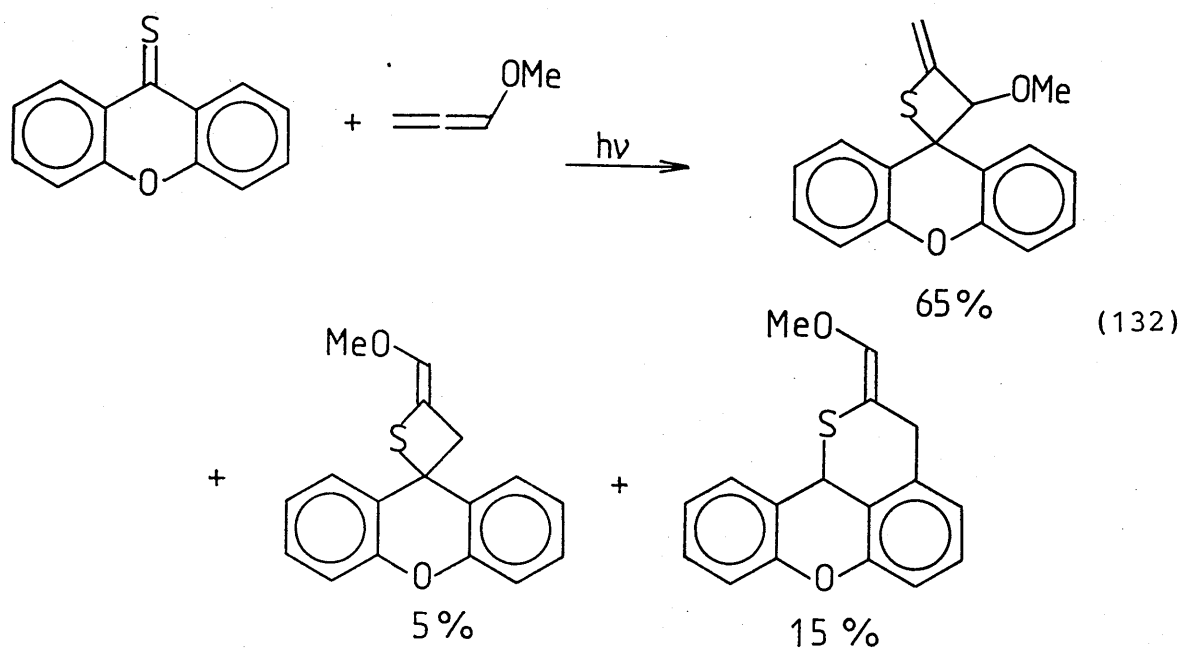
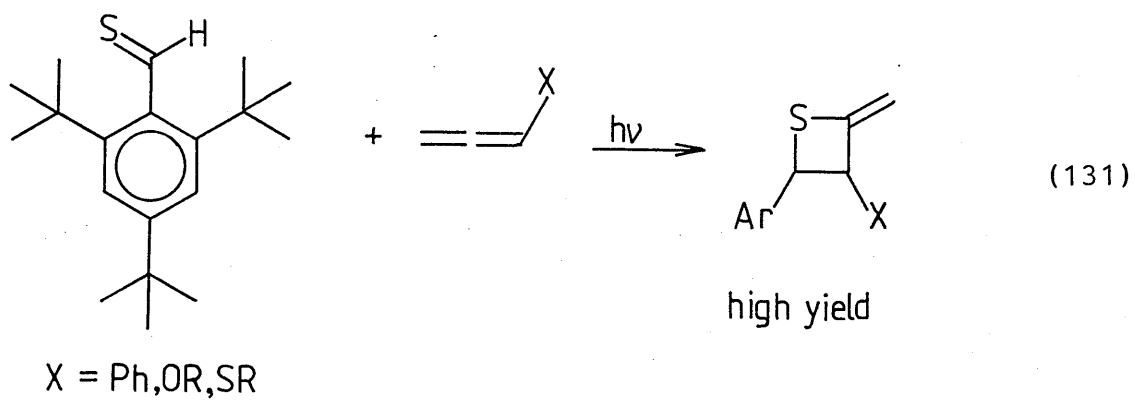


When our research into thioimides was started, no reports of work concerning the photochemistry of these compounds had been published. However following the publication of our preliminary results¹⁹³ on the photocycloaddition reactions of the thiophthalimides with alkenes, Kanaoka published results on the same subject¹¹⁰. The extent of overlap between the two pieces of work is small: reactions between N-methylthiophthalimide and trans-stilbene or 2,3-dimethylbut-2-ene are the only areas covered in both Kanaoka's work and ours, and different experimental conditions were used. In his paper, Kanaoka reports that the irradiation of alicyclic dithioimides with alkenes leads regioselectively to spirothietanes (129); similarly the irradiation of dithiophthalimides with alkenes may lead to the spirothietane or the corresponding ring-cleaved product (130).

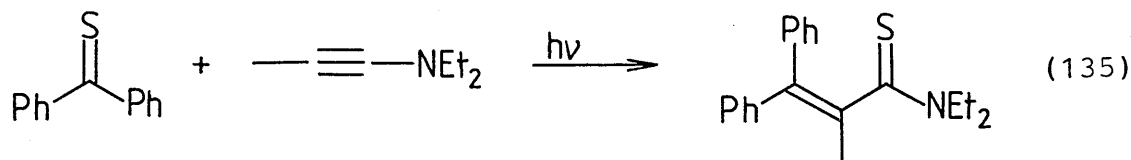
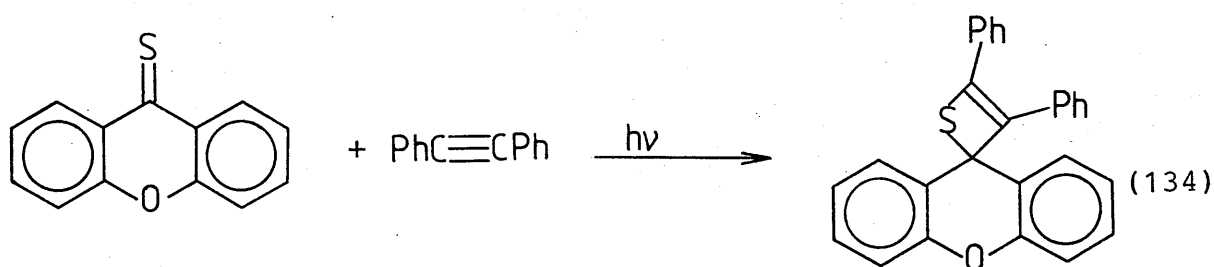


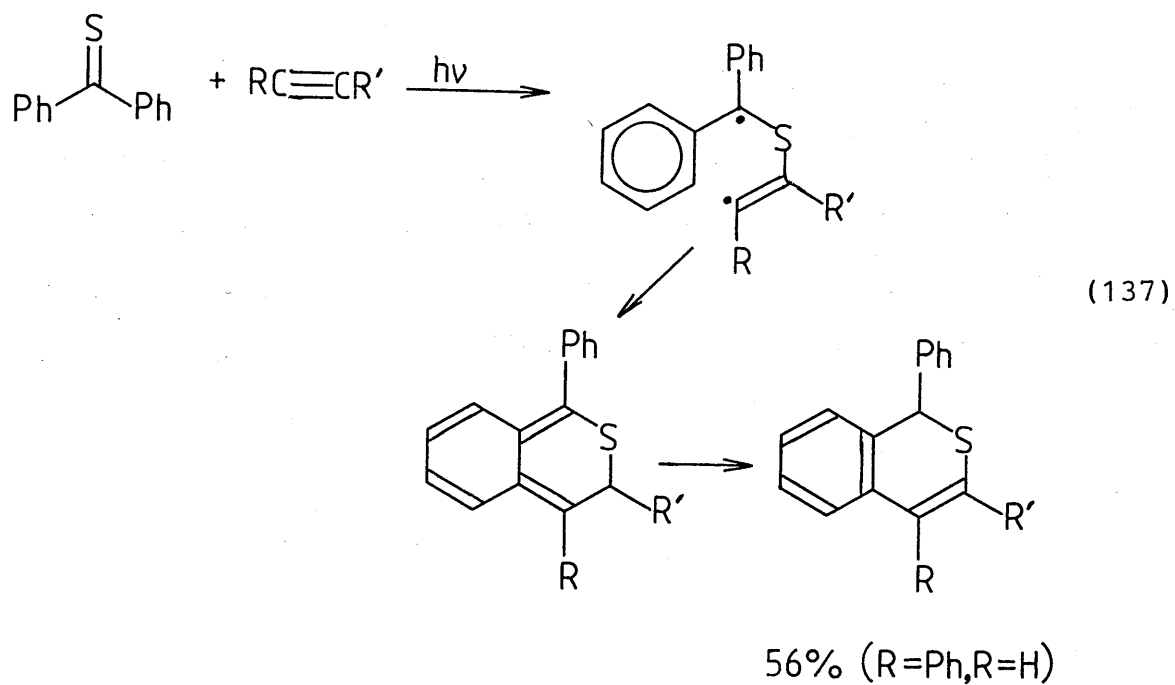
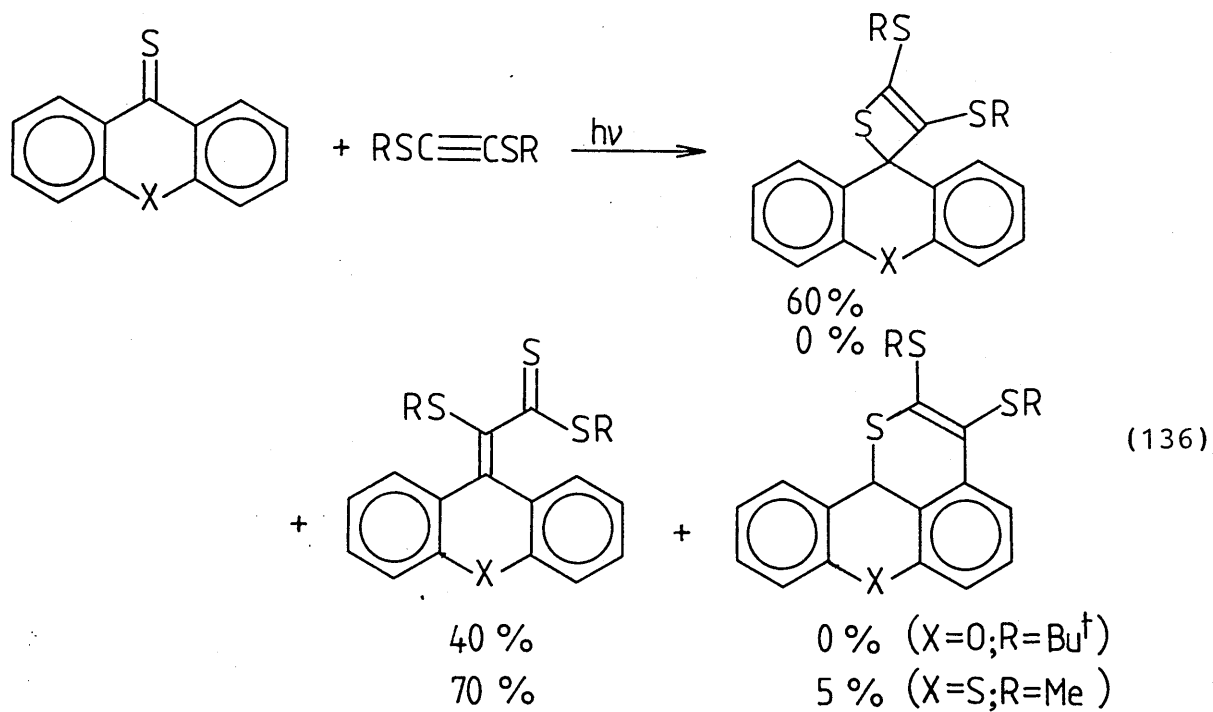


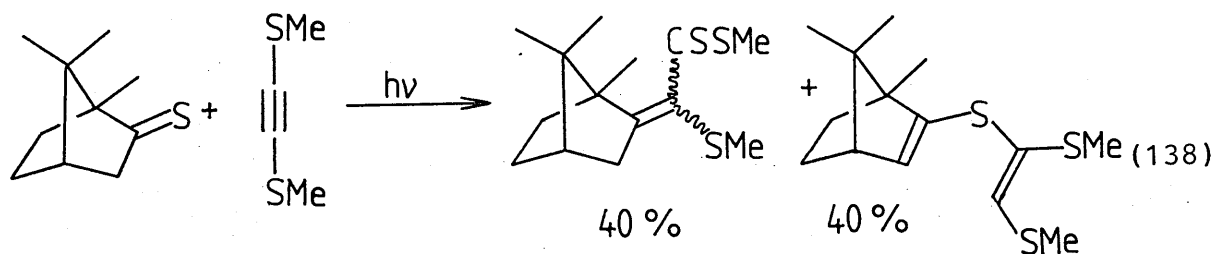
Reactions of thioketones with cumulenes have also proved fruitful. Allenes (1,2-dienes) give 2-methylene-thietanes upon irradiation with aromatic thioketones^{179,194,195} or with 2,4,6-tri-*t*-butylthiobenzaldehyde (131)¹⁹⁶. In the case of xanthione with methoxyallene the biradical intermediate reacts with one of the aromatic rings to produce an additional ring-fused product (132)¹⁹⁷. Detailed investigations into the mechanism of these reactions have shown that they occur via the triplet state of the thioketone; it has also been shown by using an optically active allene that the biradical intermediate does not disproportionate to give the starting materials¹⁹⁸. Other cumulenes have included butatrienes¹⁹⁹, pentatetraenes²⁰⁰, and a ketenimine (133)²⁰¹.



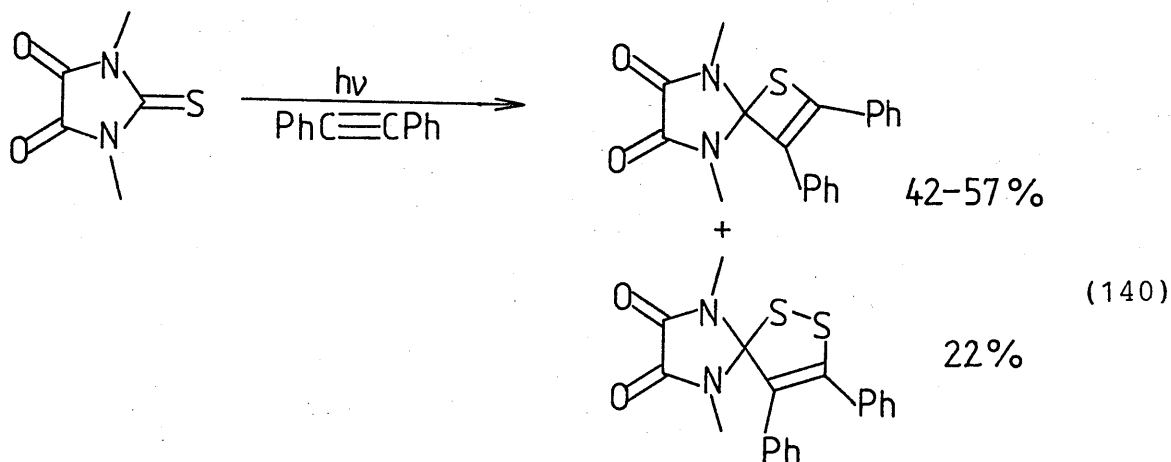
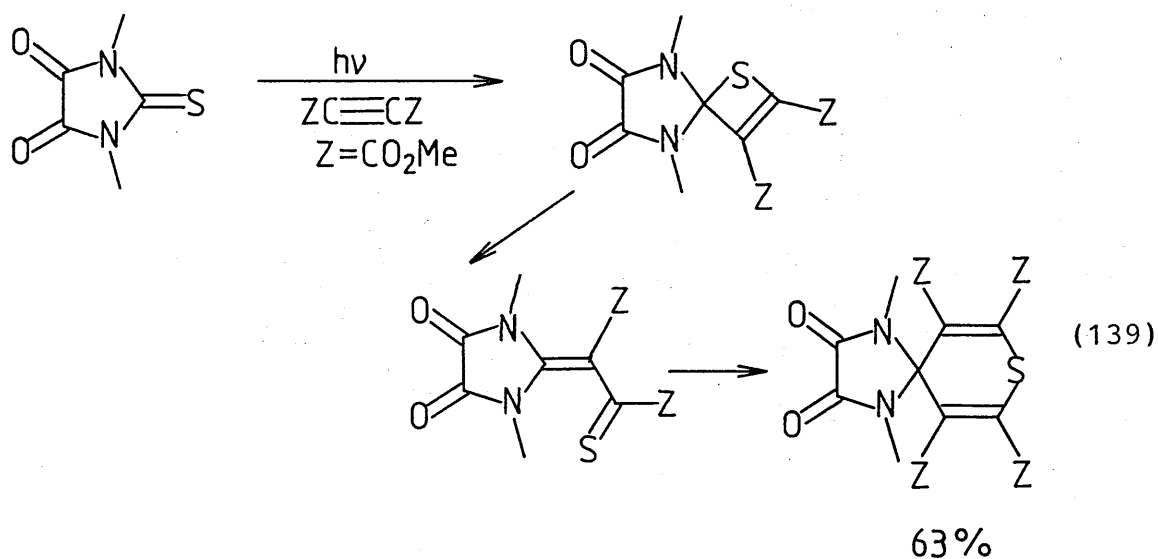
Alkynes may also undergo photocycloaddition to thio-carbonyl compounds. With diphenylacetylene and xanthione a spirothiete is obtained (134)²⁰²; in the reaction of an amino-alkyne with thiobenzophenone the initially-formed thiete ring opens to form an unsaturated thioamide (135)²⁰³. Bis(alkyl-thio)alkynes with xanthione yield an equilibrium mixture of thiete and unsaturated dithioester (136)^{204,205}, and some additional minor products also arise via internal attack of the biradical on one of the aromatic rings. In the photocycloaddition of thiobenzophenone to alkynes the major products are isothiochromenes (137)²⁰⁶; the suggested mechanism for the proposed intramolecular hydrogen transfer is supported by deuterium labelling studies. These reactions occur following excitation to S_1 , and are thought to proceed via the $T_1(n, \pi^*)$ states of the thioketones. In the reaction of thiocamphor with bis(methylthio)acetylene the intermediate biradical may undergo an alternative reaction, in which there is an intramolecular hydrogen transfer (138)²⁰⁷.



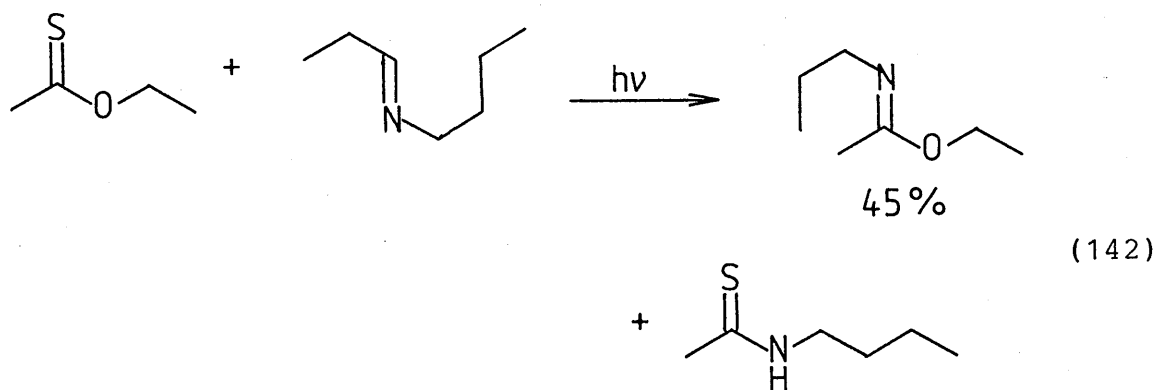
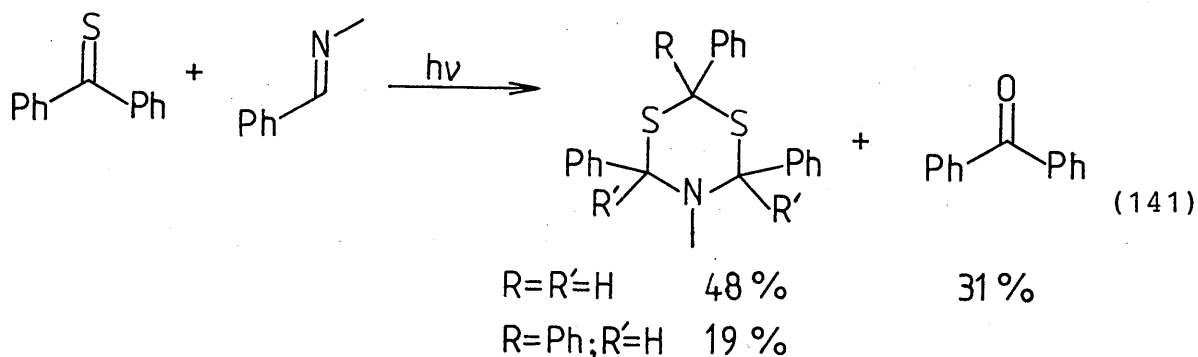


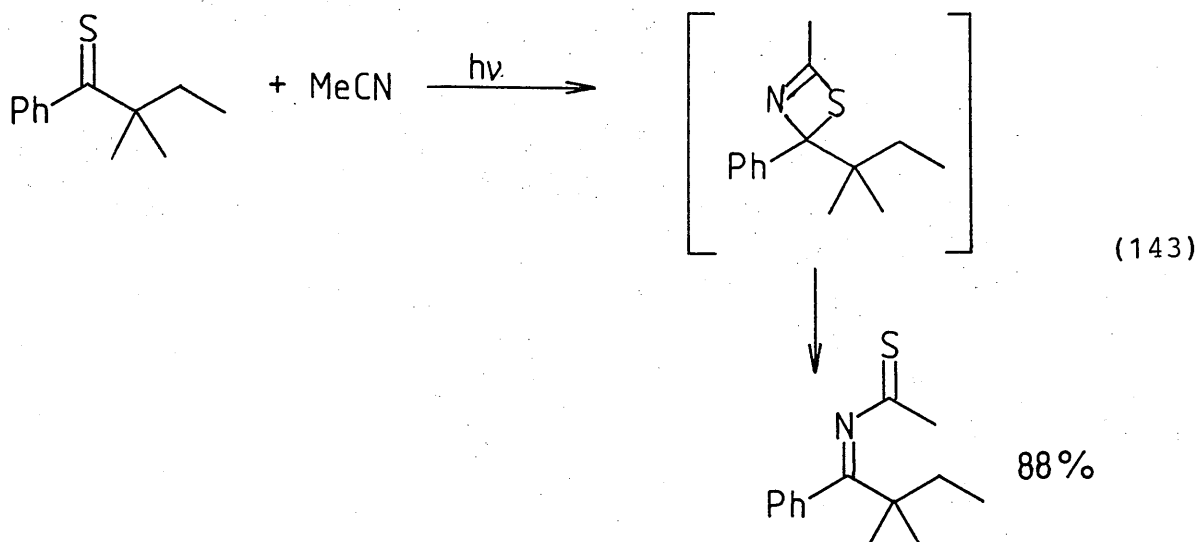


Other thiocarbonyl compounds are also known to react with alkynes. Thioparabanates give thietes, together with additional products derived therefrom, upon irradiation with suitable alkynes (139,140)^{202,208}. 1,2-Dithiole-3-thiones undergo photocycloaddition reactions with alkynes²⁰⁹, which are analogous to their reactions with alkenes.

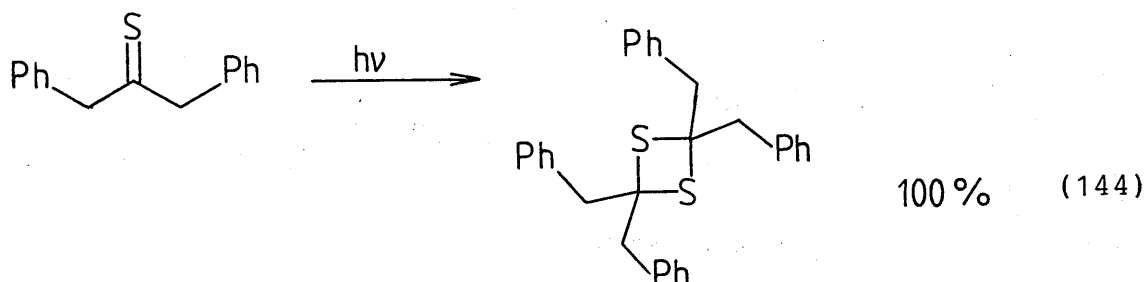


Photocycloaddition reactions of thiocarbonyl compounds to carbon-nitrogen double bonds has also received some attention. The reaction of thiobenzophenone with an aldimine gives a mixture of 1,3,5-dithiazinanes (141), which are probably formed from the breakdown products of a 1,3-thiazetidine²¹⁰; this reaction occurs following excitation to either S_1 or S_2 , although the S_2 reaction is more efficient. The reaction of an O-alkyl thioester with an imine to yield an imidate (142) probably also occurs via an intermediate 1,3-thiazetidine²¹¹. Thioketones react with nitriles, leading to N-thioacylketimine products which are thought to arise via an intermediate 1,3-thiazete (143)²¹²; it was unclear whether this reaction proceeds from T_1 or S_2 , but it was found to be more efficient following excitation to S_2 .

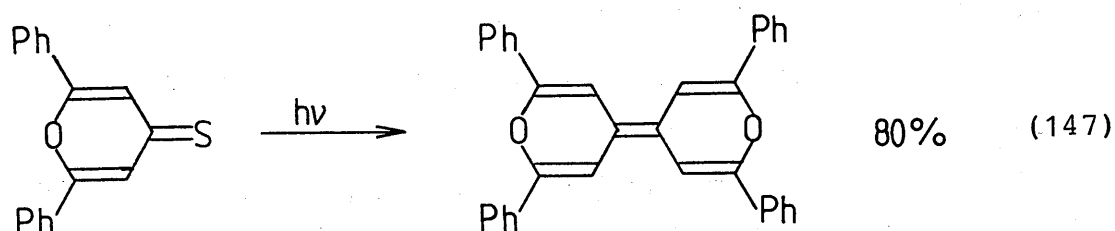
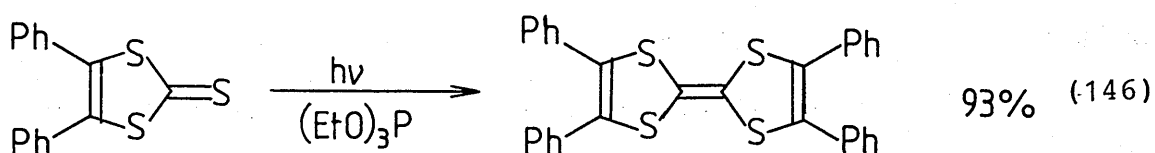
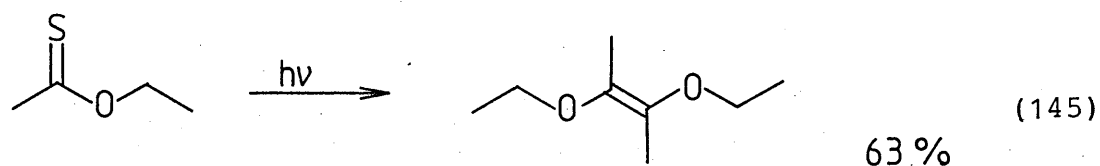




Some thiocarbonyl compounds dimerise by photocycloaddition. 1,3-Dithietanes can be isolated from irradiations of compounds such as thiophosgene²¹³, dibenzyl thioketone (144)¹²⁰, and adamantanethione¹⁴³. The dimerisation reaction of this latter follows excitation to either S_2 or S_1 .



Thiocarbonyl compounds in which the thiocarbonyl bond is relatively electron-rich tend to give 1,2-dithietanes, rather than 1,3-dithietanes, and these readily undergo loss of sulphur to give symmetrical alkenes. Thus dialkoxyalkenes can be made from α -alkyl thioesters (145)²¹¹ (although a competing reaction to give linear oligomers is also possible)¹⁰⁶; 1,3-dithiole-2-thiones give tetrathiafulvalenes (146) on irradiation²¹⁴, and pyran-4-thiones may dimerise (147)²¹⁵. However a later investigation²¹⁶ of this latter, triplet state, reaction concluded that the initial step was hydrogen abstraction from the solvent.



From the abstraction above it is clear that for phthalimides and N-substituted phthalimides many of the major mechanistic pathways begin with electron-transfer processes from the $S_1(n, \pi^*)$ state; some reactions also occur from the triplet states. By comparison there are two main types of reactions from thiocarbonyl compounds - those from the $T_1(n, \pi^*)$ state, which involve biradical intermediates, and those from the $S_2(\pi, \pi^*)$ state, which are more energetic processes for which the mechanisms are not always known in detail.

Therefore it is of interest to investigate the reactions of the thiophthalimides, to see how they compare both with the phthalimides and with the other thiocarbonyl compounds.

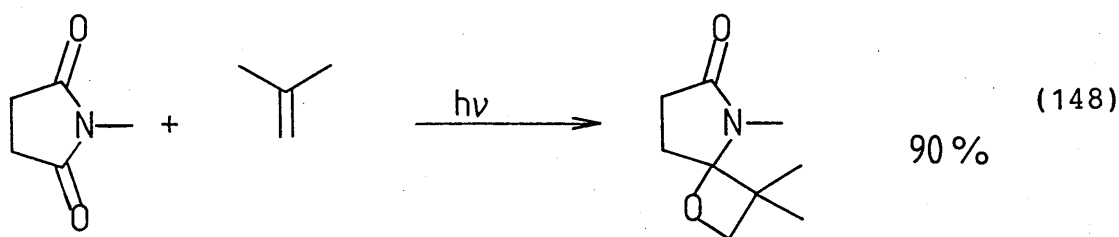
CHAPTER TWO

PHOTOCHEMISTRY OF THIOPHTHALIMIDES:

PHOTOCYCLOADDITION REACTIONS

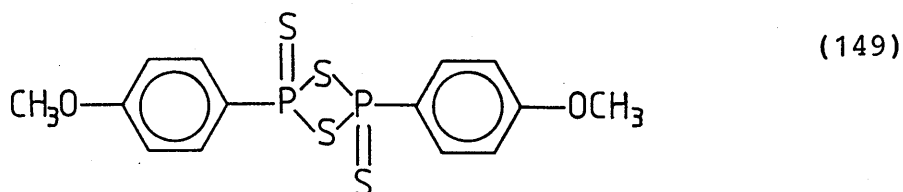
RESULTS AND DISCUSSION

Interest in the photocycloaddition reactions of thiophthalimides arises because both N-substituted imides and thioketones exhibit a range of different photocycloaddition reactions. Whereas saturated alicyclic imides, such as succinimides, lead to oxetanes upon irradiation with alkenes (148)²¹⁷, in a reaction analogous to the Paterno-Büchi reaction of ketones, aromatic imides, such as phthalimides lead to azepinediones (34). By contrast, thioketones give mainly thietanes (109). This study into the photocycloaddition reactions of thiophthalimides was carried out in order to provide a comparison with N-substituted phthalimides and with other thiocarbonyl compounds.



Almost all of the photocycloaddition reactions which we have studied involve the N-methylthiophthalimides. The preference for these compounds rather than the N-unsubstituted compounds is due to their relative ease of preparation and their solubility in a variety of solvents, and also that most of the reported intermolecular photocycloaddition reactions of phthalimides employed N-methylphthalimide. The first preparation used for N-methylthiophthalimide was a methylation of thiophthalimide²¹⁸. However this reaction gave a mixture of products, possibly due to reaction at the sulphur atom as well as at the nitrogen atom. Subsequent preparations were carried out using Lawesson's reagent for thiation of N-methylphthalimide²¹⁹, which in turn was prepared by a standard method²²⁰ from phthalic anhydride and methylamine.

Lawesson's reagent (149)²²¹ is a good general thiation reagent, which may be used for ketones, esters, amides and imides. The ratio of thiophthalimide to dithiophthalimide products may be altered by adjusting the proportion of Lawesson's reagent which is used in the reaction: for a 2:1 ratio of N-methylphthalimide to Lawesson's reagent 32-44% of N-methylthiophthalimide and 9-20% of N-methyldithiophthalimide are obtained, whereas for a 1:1 ratio of N-methylphthalimide to Lawesson's reagent 65% of N-methyldithiophthalimide is obtained.



Thiophthalimide and N-substituted thiophthalimides are orange or red in colour; N-substituted dithiophthalimides are purple-brown as crystals and yellow-brown in solution.

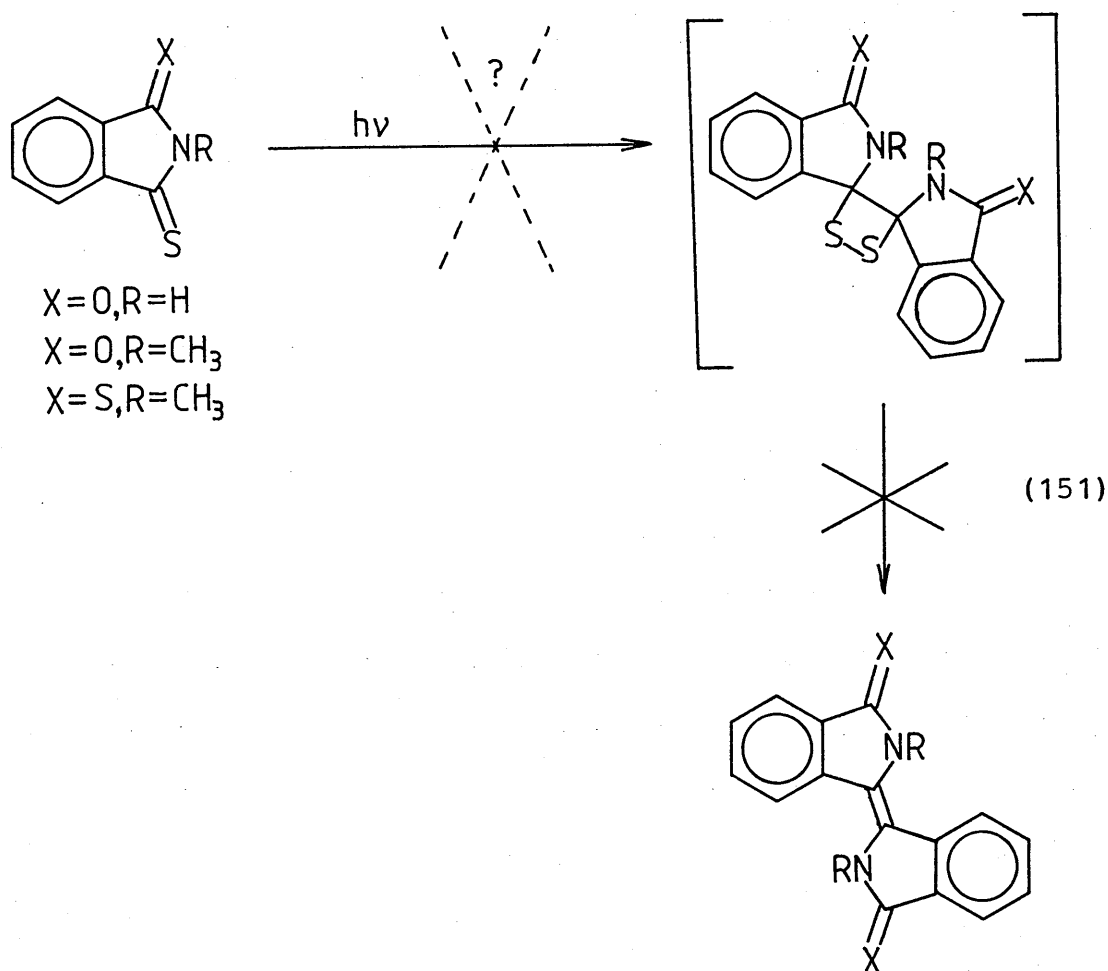
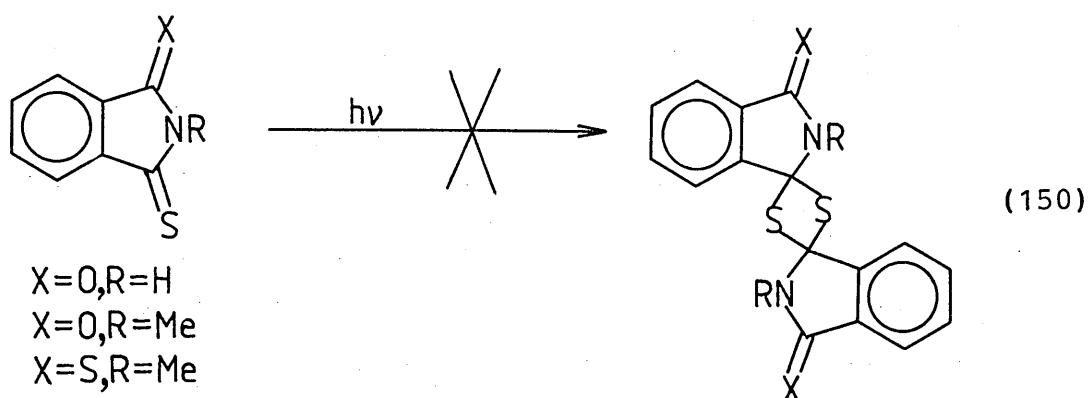
Thiophthalimide, N-methylthiophthalimide and N-methyldithiophthalimide were each irradiated alone in acetonitrile as control reactions. The first appeared almost unchanged following forty-eight hours irradiation; the additional faint spots which appeared on T.L.C. did not account for any significant amount of products, since the infrared spectrum of the crude reaction mixture was a close match to that of the unreacted starting material. Irradiation of N-methylthiophthalimide for fifty-seven hours showed N-methylphthalimide as the only product (T.L.C.).

Similarly, irradiation of N-methyldithiophthalimide for fifty hours led mainly to oxidation products. A ¹H-NMR spectrum of the crude reaction mixture showed singlets at

δ 3.40 and δ 3.15, indicating the presence of N-methylthiophthalimide and N-methylphthalimide respectively. Following recrystallisation to remove some of the unchanged N-methyl-dithiophthalimide, the mixture was separated by column chromatography; the first four fractions showed strong C=O absorptions at 1740 cm^{-1} or 1725 cm^{-1} in their IR spectra, which are also (respectively) indicative of N-methylthiophthalimide or N-methylphthalimide.

Some dark-green low R_f products were also eluted. These gave poorly resolved IR and ^1H -NMR spectra, and thus could not be characterised. The yield was approximately 25% by weight of the N-methyldithiophthalimide which had reacted. Such products were found in all of the attempted photocycloaddition reactions of N-methyldithiophthalimide.

Two other features were noted from these control irradiations. One was that no stable 1,3-dithietanes were formed (150), as might have been expected by comparison with other thiocarbonyl compounds such as adamantanethione¹⁴³ or dibenzyl thioketone (144)¹²⁰; neither were any products isolated which might have been derived from 1,2-dithietanes (151), as might have been expected by comparison with O-alkyl thioesters (145)²¹¹. The second feature was that there is no reaction between the thiophthalimides and acetonitrile leading to stable isolable products, as has been observed for some thioketones (143)²¹².



The largest range of photocycloaddition reactions in our study has been carried out with alkenes, both intermolecular examples using alkenes with alkyl, aryl or electron-withdrawing groups, and one intramolecular example. In all of these photocycloaddition reactions small amounts of

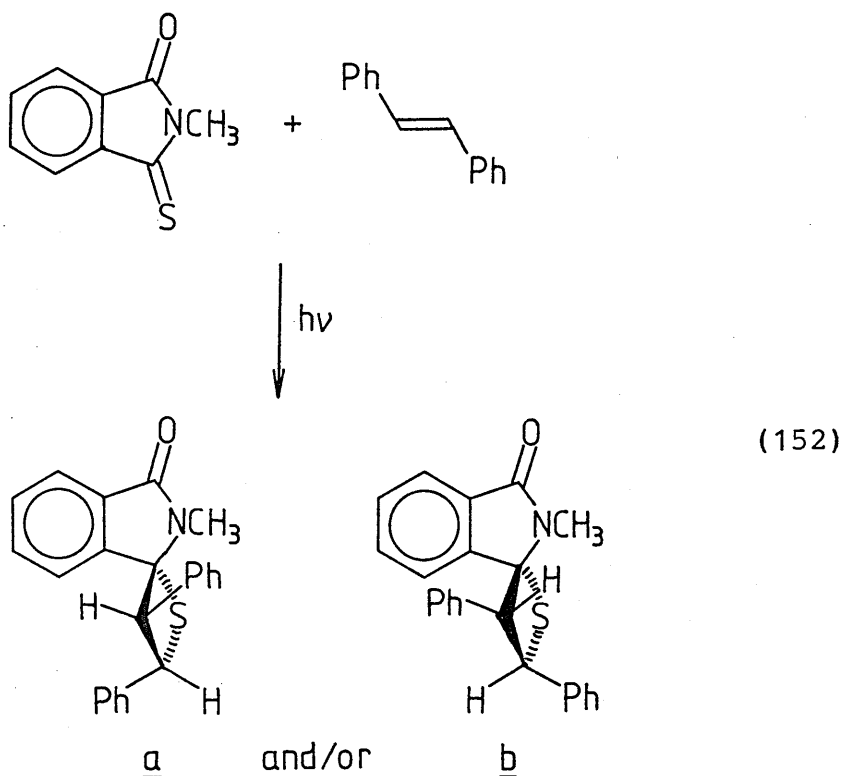
oxidation products were also formed, and the oxidation reactions will be discussed in the next chapter.

The alkene reaction that we have studied most intensively has been with stilbene. Reaction of N-methylthiophthalimide with trans-stilbene leads to a trans-thietane which can be isolated in 45% crude yield (38% after purification). A second isomer of the trans-thietane is also produced in 25% crude yield (6% after purification), in addition to the ubiquitous N-methylphthalimide.

The structure of the major thietane was established from a study of the spectral and analytical properties. The elemental microanalysis is a close fit for a 1:1 N-methylthiophthalimide : stilbene adduct. The integrity of the carbonyl group is shown by the strong absorption in the IR spectrum at 1708 cm^{-1} , and the weak absorption in the ^{13}C -NMR at 167.5 ppm. The ready loss of $\text{PhCH}=\text{S}$ from the molecular ion in the mass spectrum shows the stilbene moiety to be attached to the sulphur atom. The doublets at 5.53 and 5.42 ppm in the ^1H -NMR spectrum would be consistent with the stilbene moiety being incorporated into a spiro-thietane ring; the ^{13}C -NMR absorptions at 62.0 and 42.7 ppm would also be consistent with such a structure. The quaternary ^{13}C -NMR absorption at 73.0 ppm is in the region expected for the carbon at the spiro-junction.

The trans orientation of the phenyl groups in the major isomer of the thietane is indicated by ^1H -NMR, in which the coupling constant of the thietane protons is 11 Hz; a cis-orientation might be expected to show a coupling constant of around 2-5 Hz. The best ^1H -NMR spectrum of the minor isomer

appears to show a coupling constant for the thietane protons of 15 Hz; however it was not possible to obtain full NMR spectral characterisation for this compound on account of its insolubility in most of the common solvents. It is not possible to determine from the spectral data whether the major isomer is the trans-thietane (152a) or (152b). The former structure seems more likely on steric grounds as the 3'-phenyl is not in close proximity to the phthalimide aromatic ring as it is in (152b).



Following our work Kanaoka has also published an account of this reaction¹¹⁰, but using a high-pressure lamp for a shorter time, in which he reports the isolation of two products in 36% and 44% yields respectively. The first clearly corresponds to our major isomer, and the second is possibly our minor isomer, as it is a 1:1 adduct. However, the mass spectra (m/z 235 (M^+ -PhCHS) for the reported product, and m/z 325 (M^+ -S) for our product) and the melting temperatures (206-

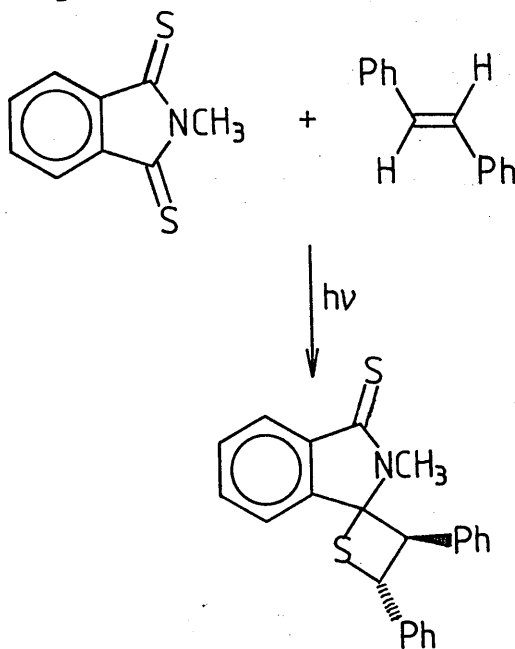
209 °C for the reported product, and 235-238 °C for our product) of the second products suggest that they are of different composition. However, the ^{13}C -NMR spectrum (d_6 -acetone) of Kanaoka's product²²² 29(b), which shows absorptions at 166.4, 140.1, 131.8, 131.6, 130.3, 130.2, 129.6, 128.7, 128.1, 127.4, 124.1, 122.1, 71.6, 45.1 and 24.9 ppm resembles that of our product (also using d_6 -acetone as solvent), which shows absorptions at 166.2, 141.8, 131.9, 131.8, 130.2, 130.1, 129.5, 128.5, 128.0, 127.7, 127.4, 124.1, 122.2, 108.2, 71.8, 45.0 and 24.4 ppm. (Neither of the two compounds were pure; both showed other small absorptions.) In addition, the ^1H -NMR spectrum of Kanaoka's product 29(b), which is taken in CDCl_3 solution and shows absorptions at δ 7.8-6.6 (m, 14H), δ 5.45 (d, J = 10 Hz, 1H), δ 5.15 (d, J = 10 Hz, 1H) and δ 3.45 (s, 3H), is comparable with that of our product, taken in d_3 -acetonitrile solution, which shows absorptions at δ 7.95-7.75 (m, 1H), δ 7.75-7.25 (m, 9H), δ 7.25-6.80 (m, 5H), δ 5.68 (d, J = 16 Hz, 1H), δ 4.97 (d, J = 16 Hz, 1H) and δ 3.35 (s, 3H). Although the infrared spectrum for his 29(b) is somewhat unclear, it shows a carbonyl absorption at 1698 cm^{-1} (nujol mull), which is within the error limits of that of our product, at 1710 cm^{-1} (KBr disc), and so it is possible that the two products may be of the same composition.

An additional minor product was obtained in small quantity when we repeated the reaction in order to investigate the minor products further, but only an infrared spectrum was obtained.

The reaction of N-methyldithiophthalimide with trans-stilbene leads to the formation of a trans-thietane in 65%

crude yield, though purification proved difficult and led to only 13% of pure product. The structure was shown to be a trans-thietane by the spectral and analytical data. The elemental microanalysis showed the product to be a 1:1 N-methyldithiophthalimide : stilbene adduct, and the analogy between this product and the trans-thietane (major isomer) from the reaction of N-methylthiophthalimide and trans-stilbene is shown by a comparison of the ^1H -NMR spectra, in which the chemical shifts (with the exception of the N-Me singlet at $\delta 3.41$, which would be expected to be at lower field on account of its proximity to the thiocarbonyl group) and multiplicities are closely similar. The ^{13}C -NMR spectrum also appears similar, but with an absorption at 193.2 ppm, corresponding to an unreacted thiocarbonyl group, rather than at ~ 167 ppm, which would be appropriate for an unreacted carbonyl group.

The trans-stereochemistry was assigned on the basis of a coupling constant of 11 Hz seen for the thietane protons in the ^1H -NMR spectrum. The minor products (including oxidation products) were not characterised as they were all obtained as mixtures in small quantities.



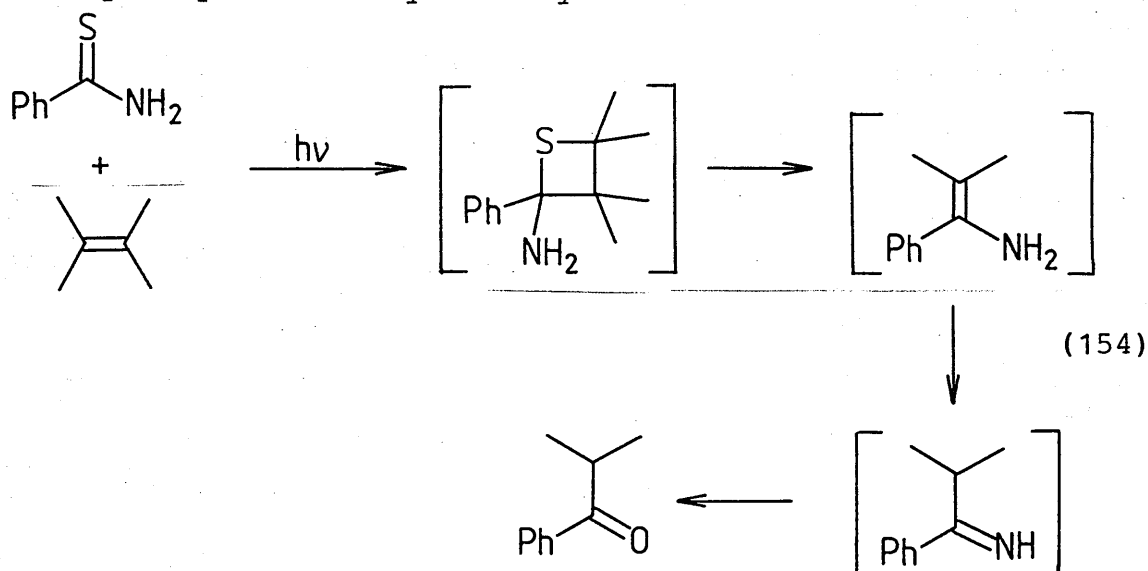
(153)

These reactions described above were carried out using a medium-pressure mercury lamp and a Pyrex filter. The reactions were also tried using white light from a 60W tungsten bulb and with either dichloromethane, dichloromethane with a few drops of pyridine, or benzene as solvents; the choice of dichloromethane with the addition of a small quantity of pyridine as a solvent was suggested by Bos and Kamphuis¹⁹⁸ following their photocycloaddition experiments with allenes and thioketones, in which it was found that the use of a slightly basic solvent prevented breakdown of the thietane products. In dichloromethane the monothioimide appeared to give smaller amounts of minor products than in benzene (as judged by T.L.C.), although ¹H-NMR spectra of the three samples were not greatly different. However, it was noted that a white precipitate had formed in benzene, which proved to be insoluble in deuteriochloroform. An infrared spectrum showed this precipitate to be identical to the minor trans-thietane isomer which had been isolated previously.

In the white-light reactions for N-methyldithiophthalimide and trans-stilbene the same products were formed in all solvents, but the distribution of the minor products varied between the benzene and dichloromethane solutions, as judged by T.L.C. and ¹H-NMR.

An irradiation of unsubstituted thiophthalimide with stilbene led to a mixture of products. Despite chromatographic separation and repeated attempts at recrystallisation no pure compounds could be isolated. However it is possible that some thietane products were formed, since there were multiplets at δ 4.20 and δ 5.40 in some of the product ¹H-NMR spectra and saturated aliphatic absorptions in the ¹³C-NMR spectra. For the

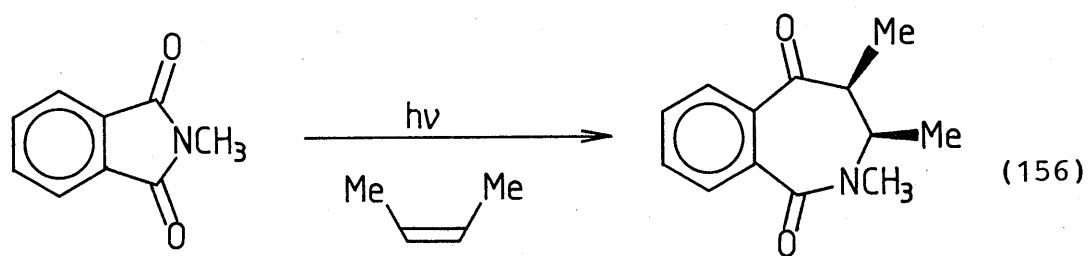
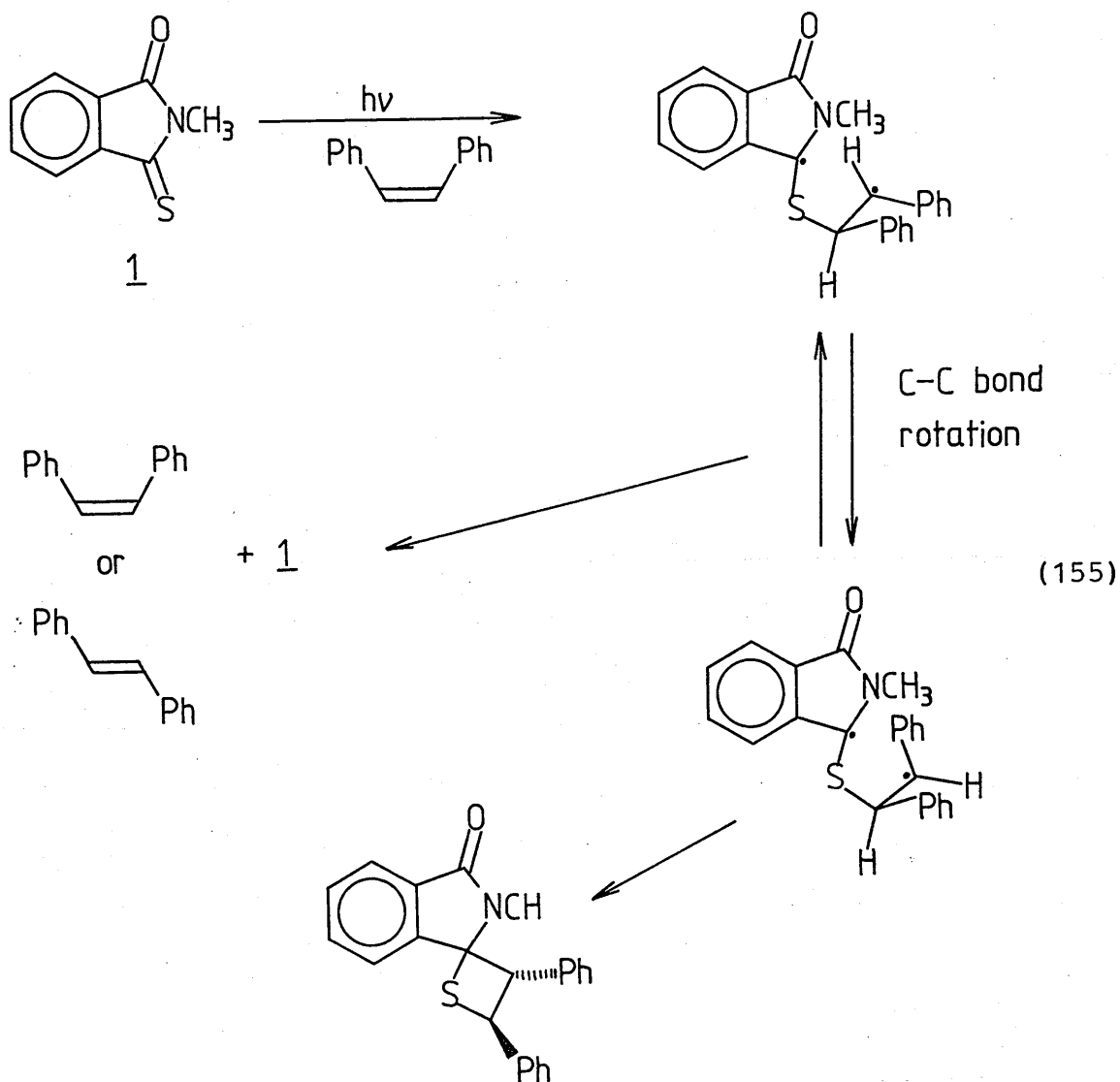
former, such multiplets are not accounted for by starting materials or solvents, and the chemical shift values are consistent with those seen for the thietane protons in the products from N-methylthiophthalimides with stilbene. For the ^{13}C -NMR spectra, such absorptions are not accounted for by starting materials, for which all absorptions have a chemical shift in excess of 100 ppm, and would not all be accounted for by solvents; the chemical shift values are consistent with those seen for the 3' and 4' carbon atoms of the above-mentioned thietanes. It is possible that there are competing reactions involving the hydrogen atom of the -NH group, which makes the situation different from that for N-methylthiophthalimide. Kanaoka et al have reported¹³⁵ that the photocycloaddition of 2,3-dimethylbut-2-ene with thiobenzamide in a nitrogen atmosphere leads to a product derived from the breakdown of a thietane (154), although we have no evidence to suggest that a similar thioimide-derived thietane should decompose particularly readily.



To investigate the stereoselectivity of the reaction with stilbene, N-methylthiophthalimide was irradiated with cis-stilbene. The products were the same trans-thietanes as from

the reaction with trans-stilbene (confirmed by a comparison of the ^1H -NMR spectra, infrared spectra or melting temperatures) in 34% and 1% yields respectively. A lower R_f fraction contained a mixture of products, possibly including 2:1 N-methylthiophthalimide : stilbene adducts, as there are singlets near $\delta 2.0$ and a multiplet around $\delta 4.4$ in the ^1H -NMR spectrum (see later for a discussion of 2:1 adducts in the reaction of N-methylthiophthalimide with styrene). The stilbene which was recovered from the mixture was partly isomerised: from the ^1H -NMR spectrum it was possible to estimate the proportions of cis- and trans-stilbene to be approximately 60% cis- and 40% trans-isomer.

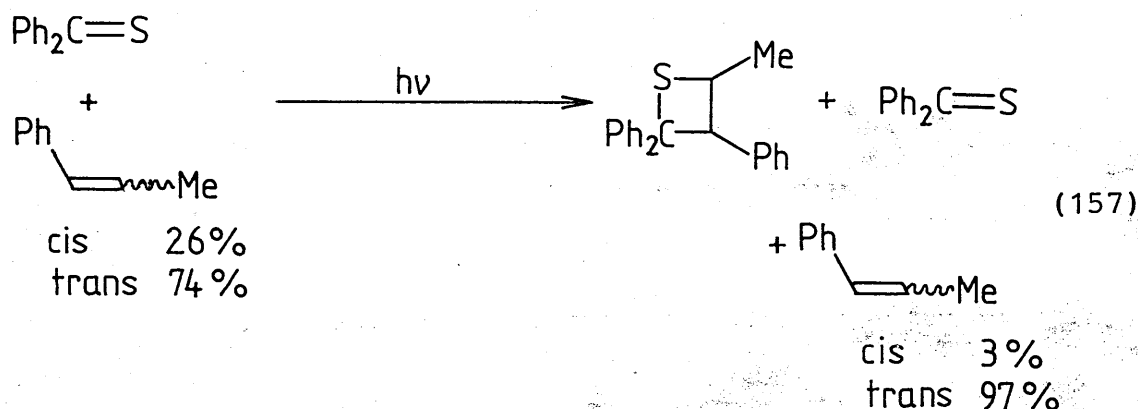
Two conclusions may be drawn from these results. First, the reaction is non-stereospecific, which implies that there is some mechanism by which the stereochemistry is lost. One possible intermediate which may be proposed for this reaction is a 1,4-biradical; if rotation about the C-C bond derived from the alkene is fast with respect to ring-closure, then cis-stilbene could lead to the thermodynamically more stable trans-product (155). The lack of stereospecificity contrasts with the reactions of N-methylphthalimide with alkenes to form benzazepinediones, in which stereoselectivity may be greater than 95% (156)⁴⁶, and it is also unlike the reactions from the S_2 state of thioketones, e.g. adamantanethione with fumaronitrile⁷⁸, which are also stereoselective. The possibility of exciplex formation (as a mechanism for the photocycloaddition of N-methylthiophthalimides with stilbene) may not be ruled out, but if it does take place then the exciplex would have to be fairly long-lived; an exciplex which collapsed immediately to form a product would give a stereoselective reaction.



The other conclusion which may be drawn is that some of the intermediate which is formed breaks down to give N-methylthiophthalimide and stilbene; this accounts for the trans-stilbene which was found in the product mixture. The presence

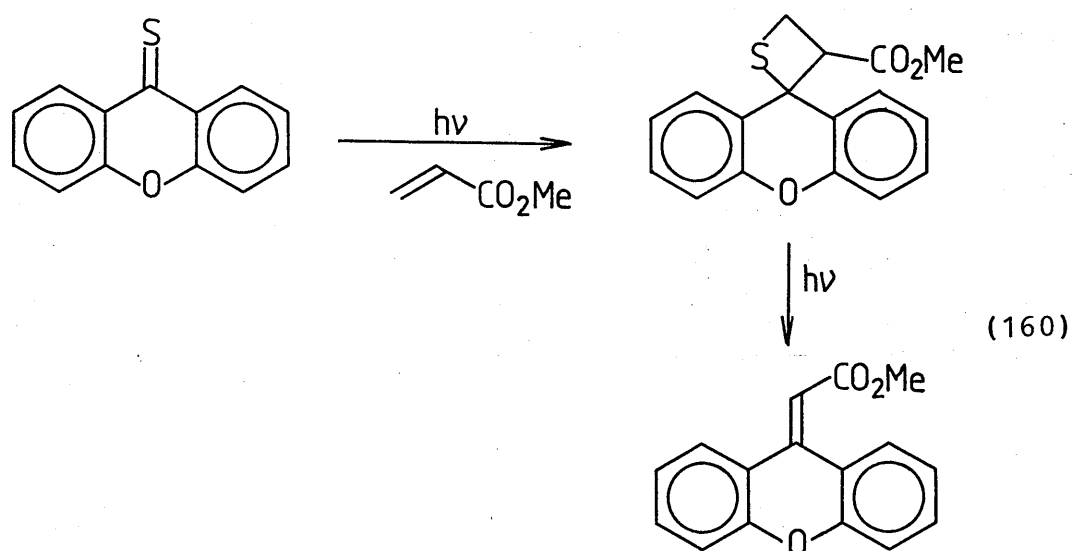
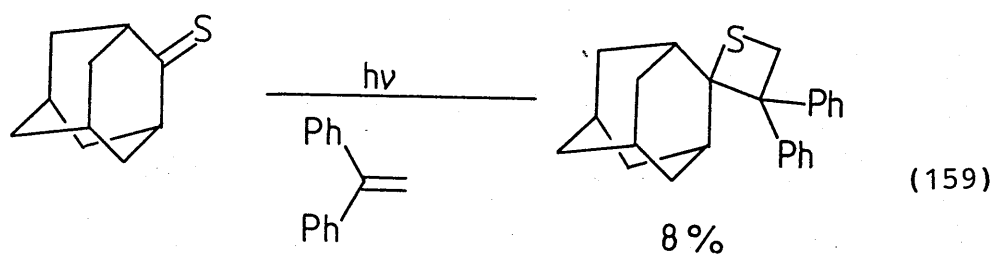
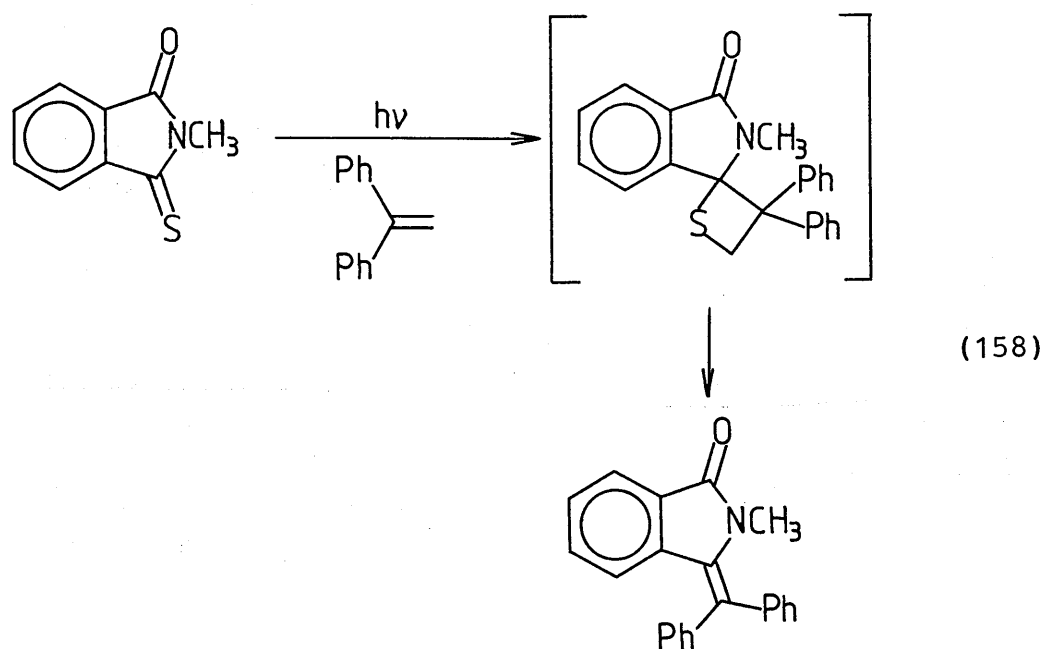
of trans-stilbene suggests that the intermediate breaks down after C-C bond rotation has occurred. It is not possible for the stilbene to isomerise directly under the experimental conditions, in which a filter solution was used, cut-off around 480 nm: neither cis- nor trans-stilbene absorb at wavelengths longer than 350 nm. As the triplet energy of cis-stilbene²²³ is 250 kJ mol^{-1} , and that of N-methylthiophthalimide is 217 kJ mol^{-1} (if the emitting state is taken to be a triplet state - see Chapter Four), isomerisation should not occur via energy transfer. However energy transfer cannot be ruled out for trans-cis-isomerisation, as the triplet energy of trans-stilbene is 208 kJ mol^{-1} .

The reaction with stilbene has some parallel with the reaction of thiobenzophenone with 1-phenylprop-1-ene, in which excitation to the $S_1(n, \pi^*)$ state leads to a thietane product and some isomerisation of the recovered alkene (157)¹⁶⁶.



To investigate the effect of alkene structure on the reaction the N-methylthiophthalimides were irradiated with 1,1-diphenylethene. For N-methylthiophthalimide a diphenylmethylene product was obtained (158) in 62% crude yield (48% after purification). The diphenylmethylene structure was indicated by the mass spectral and microanalytical results;

the elemental microanalysis gave $C_{22}H_{17}NO$ as the empirical formula, and the mass spectrum showed that the highest mass ion also corresponded to this formula. The presence of fourteen aromatic protons was indicated by the 1H -NMR spectrum, together with a $-NCH_3$ singlet at $\delta 2.89$. Both IR and ^{13}C -NMR spectra showed the presence of an intact carbonyl group. The 1H - and ^{13}C -NMR spectra also showed that there was no thietane structure (no protons or carbon atoms at positions which would be expected for a thietane, nor any absorption which would correspond to a spiro-junction carbon atom). A minor product was formed that could not be successfully isolated. The most likely route to the major product is via a spiro-thietane, but it is not possible to tell from the experimental evidence whether the breakdown of such a thietane (with elimination of thioformaldehyde) would be thermal or photochemical. A precedent exists for the formation of thietanes from this alkene with thiocarbonyl compounds, in the $T_1(n,\pi^*)$ reaction of adamantanethione with 1,1-diphenylethene (159)⁷⁸. A precedent for the elimination of $H_2C=S$ from a thietane is provided by the reaction of xanthione with methyl acrylate, in which a (methoxycarbonyl)methylene product is obtained (160)¹⁷³.



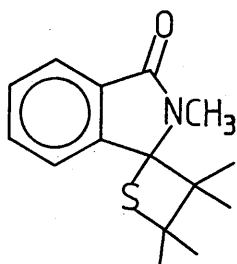
The reaction of N-methyldithiophthalimide with 1,1-diphenylethene using a medium-pressure mercury arc and a

Pyrex filter yielded two product fractions and some dark-green low R_f material after silica-gel chromatography. However closer investigation of these product fractions by infrared spectroscopy suggests that they were oxidation products rather than photocycloaddition products: all of the product fractions showed strong carbonyl absorptions. This reaction was repeated using a high-pressure mercury arc and a filter solution with a cut-off of approximately 480 nm. T.L.C. of the product mixture showed the formation of several products, but infrared and ^1H -NMR spectra showed that the main components of the mixture were unreacted starting materials and oxidation products. Some dark-green low R_f material was again formed.

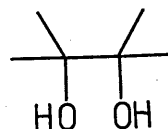
As much of the attention which has been given to the photocycloaddition of N-methylphthalimide with alkenes has been focussed on alkyl-, rather than aryl-, substituted alkenes, it is of interest to investigate the behaviour of the N-methylthiophthalimides with such alkenes. N-Methylthiophthalimide was irradiated in 2,3-dimethylbut-2-ene using a medium-pressure mercury arc and a Pyrex filter. The reaction mixture decolourised after two hours. Separation by column chromatography gave three fractions, the first of which included unreacted N-methylthiophthalimide and at least one high R_f product; further separation attempts of this fraction proved unsuccessful. The second was the major product, the thietane (161) in 22% yield. Evidence that this was a spiro-thietane arose from the ^1H -NMR spectrum, which showed four aromatic protons and five methyl singlets. Both the infrared and ^{13}C -NMR spectra showed the presence of a carbonyl group; the ^{13}C -NMR spectrum also showed a quaternary carbon atom at 93.9 ppm. The highest mass ion at 187.099, arising from loss of

$(\text{CH}_3)_2\text{C}=\text{S}$, in the mass spectrum was indicative of a thietane structure.

The third fraction was pinacol (162), which was characterised by comparison with an authentic sample; this is thought to have been an impurity from the 2,3-dimethylbut-2-ene - although the alkene was distilled before use, one impurity was observed to be present (T.L.C.), and a repeated reaction (below) using a fresh sample of 2,3-dimethylbut-2-ene did not give pinacol on separation of the reaction mixture.



(161)



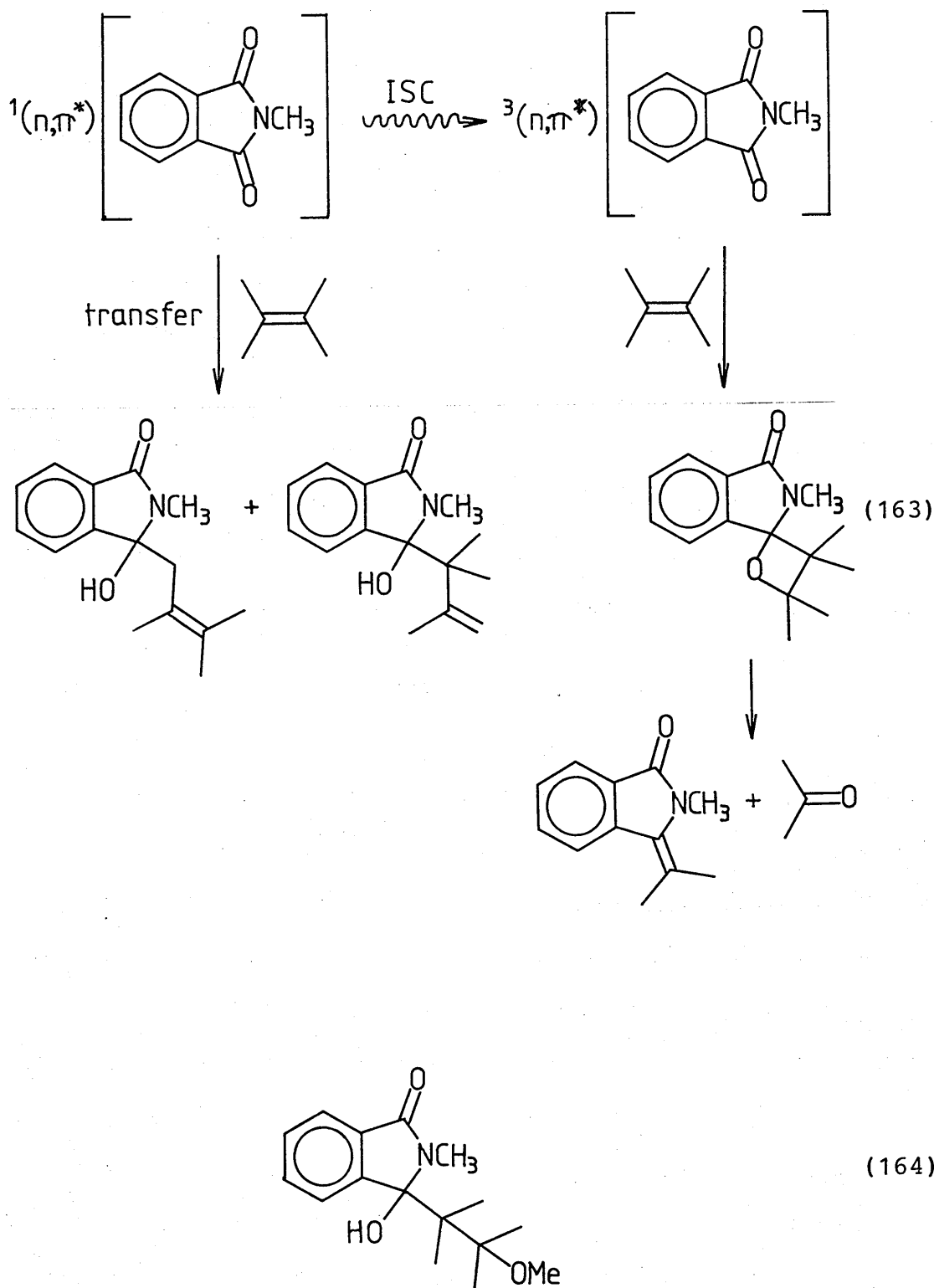
(162)

The reaction was repeated with acetonitrile as a solvent. A ^1H -NMR spectrum of the product mixture showed that a number of products had been formed. Separation by column chromatography gave several mixed fractions. The first contained unreacted starting material together with a product derived from 2,3-dimethylbut-2-ene. However this high- R_f product did not appear to be the same (^1H -NMR) as the high- R_f product which was observed in the previous experiment. All other fractions contained mixtures of products, as judged by ^1H -NMR. Some aliphatic products appeared to be present in this experiment. The largest column fraction was separated on a second column, but this did not yield any pure compounds. The thietane product was observed to be present (^1H -NMR) in three of these mixed fractions. The conclusion which may be drawn from this experiment is that the reaction in acetonitrile solution leads

to a greater range of products than that which takes place in undiluted 2,3-dimethylbut-2-ene.

2,3-Dimethylbut-2-ene does not seem to be a popular choice of alkene for reactions with other thiocarbonyl compounds. Compounds with which it has been successfully reacted are thiobenzamide¹³⁵, diphenyl thiocarbonate¹⁷⁸, thiophosgene¹⁷⁸, 1,2-dithiole-3-thiones^{224(a)} and 1,2,4-dithiazole-3-thiones^{224(a)}. The solvents for the latter four reactions were benzene or acetone, whereas that for the first reaction was not reported. Most of these reactions lead to thietane type products. With the appearance of the very recent report of Kanaoka¹¹⁰ it is possible to make a direct comparison with the reaction of N-methylthiophthalimide and 2,3-dimethylbut-2-ene in benzene, in which the product is the thietane (161) in 60% yield: it appears that in a non-polar solvent - benzene or 2,3-dimethylbut-2-ene - the thietane product predominates, whereas in acetonitrile there are competing reactions which lead to other products in addition to the thietane.

The reaction of the all-oxygen analogue, N-methylphthalimide, with 2,3-dimethylbut-2-ene in acetonitrile suggests that there are two competing processes following excitation to $S_1(n, \pi^*)$, and that the reaction scheme may be summarised as below (163)^{42,43}. In a solvent such as methanol a solvent-incorporated product (164) from the electron-transfer reaction may also be observed.

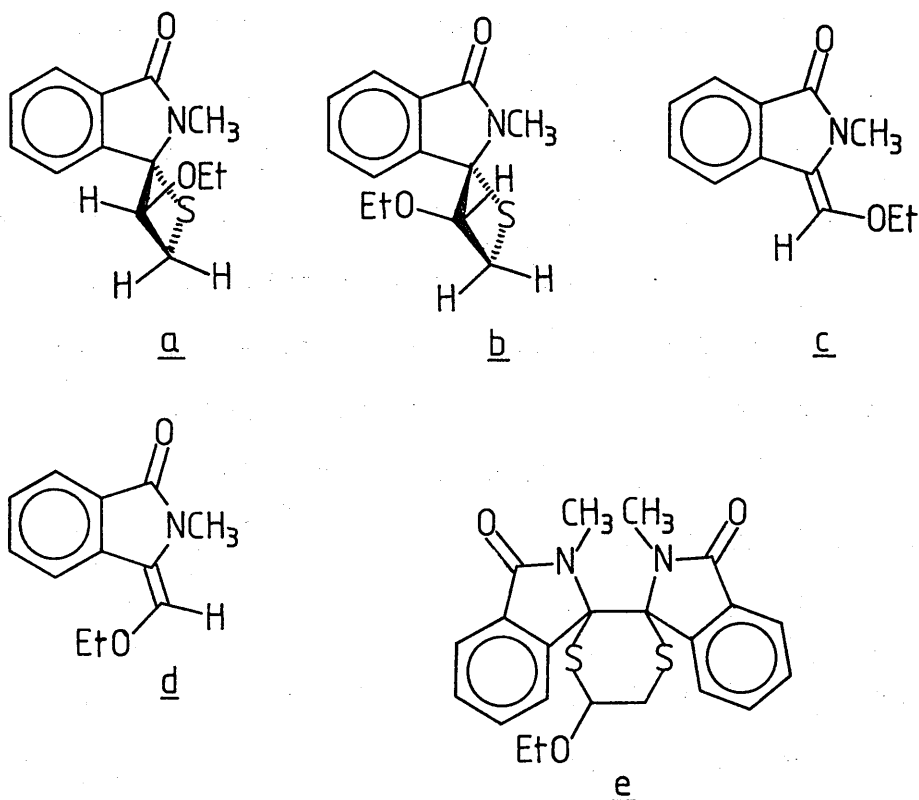


A second alkyl-substituted alkene employed was methylenecyclohexane; reaction with N-methylthiophthalimide led to a mixture of products which was difficult to separate and from which no completely pure compounds could be isolated. Due to loss of methylenecyclohexane in the nitrogen stream only 22% of the N-methylthiophthalimide had actually reacted, and so

the quantity of product mixture was not large. The purest compound isolated appeared to be a 2:1 adduct (two N-methylthiophthalimide to one methylenecyclohexane). The strongest evidence for a 2:1 adduct came from the elemental microanalysis, which is appropriate for a 2:1 adduct, but would not be for a 1:1 adduct. The ^{13}C -NMR spectrum shows two carbonyl absorptions around 170 and 172 ppm; the sharp melting temperature suggests however that this is a single compound and not a mixture. The ^1H -NMR spectrum gives an integration which is closer to that expected for a 2:1 adduct than that for a 1:1 adduct, and also shows two -NMe absorptions at δ 3.93 and δ 4.07; these values are consistent with the chemical shifts for other 2:1 adducts (described later), and would be rather high frequency for a 1:1 thietane adduct, in which the range is approximately 2.50-3.50 ppm. The mass spectrum gives no parent ion which would match either a 2:1 or a 1:1 adduct, and the highest mass peak is at 240, which is consistent with either. The infrared spectrum shows a carbonyl absorption and some aromatic absorptions. If this is a 2:1 adduct, the yield of the nearly pure material is 5%.

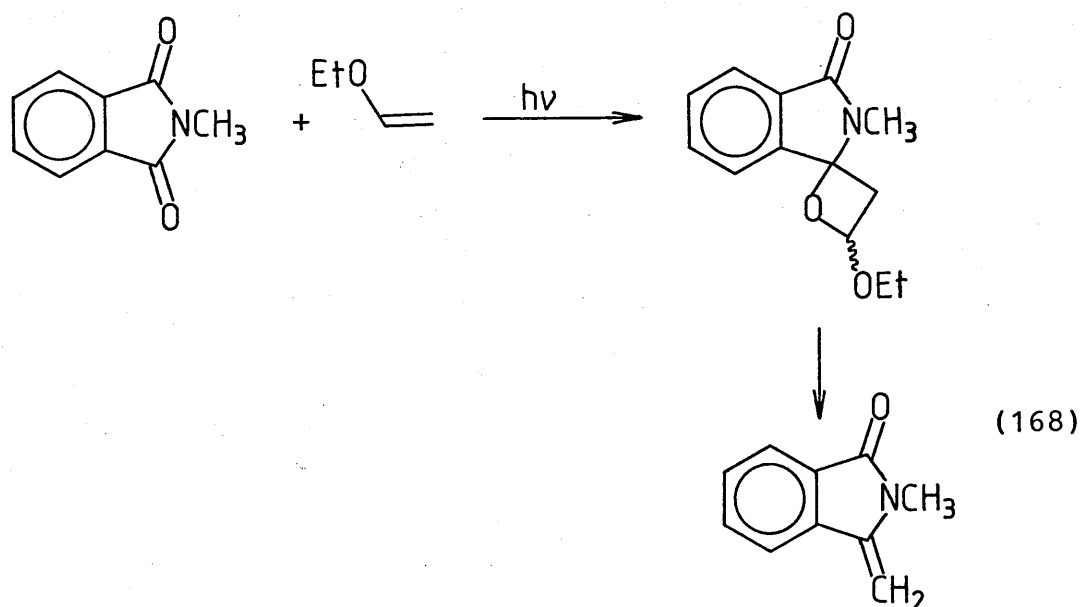
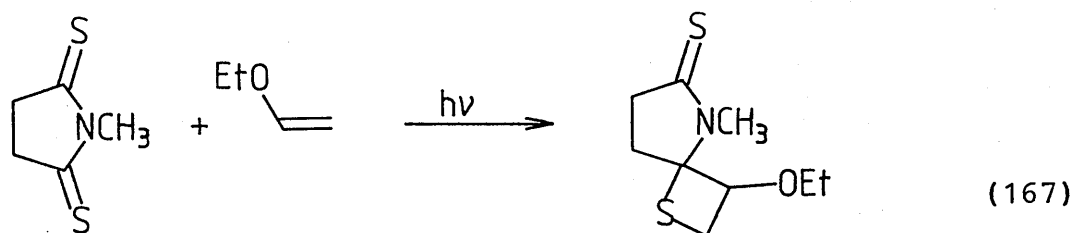
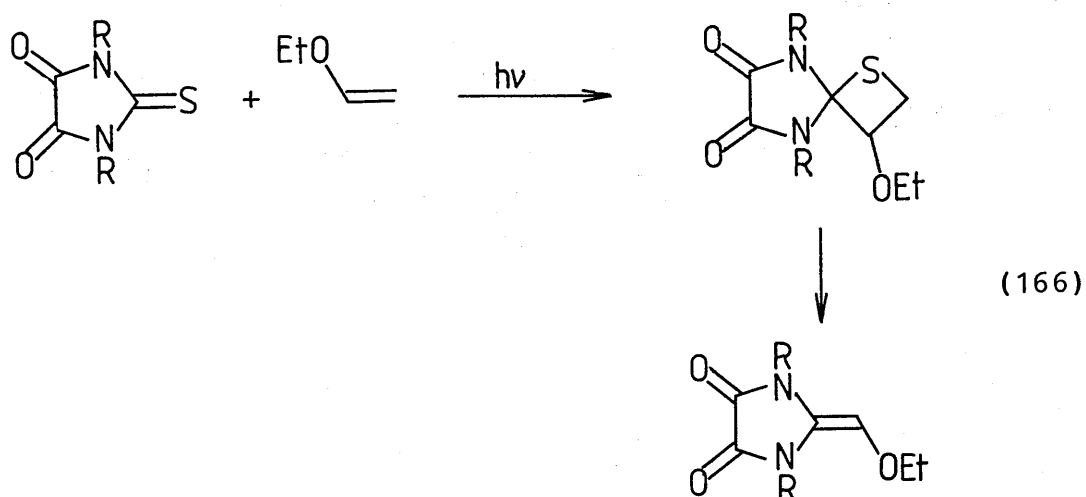
Another electron-rich alkene with which we irradiated N-methylthiophthalimide is ethyl vinyl ether; this too gave a mixture of products which was difficult to separate. The first product fraction from the silica column was N-methylphthalimide, and the second a mixture which included N-methylphthalimide. The third, larger fraction was a mixture of products which appeared to include a thietane (165a or b) as indicated by multiplets at δ 5.25 and δ 5.05 in the ^1H -NMR spectrum, and possibly also a methylene product (165c or d) derived therefrom, as indicated by multiplets around δ 6.00 in the ^1H -NMR

spectrum. There are two singlets at $\delta 2.14$ and $\delta 2.08$ which could arise from a 2:1 adduct (165e) of the same orientation as that from the styrene experiment (see later). Other signals from N-methyl groups are at rather low chemical shift, $\delta 3.87$ and $\delta 3.92$, which could be on account of proximity to the lone pair of an oxygen substituent on a thietane, or could signify a 2:1 adduct (as for methylenecyclohexane). However, further purification work on this failed to yield any pure products.

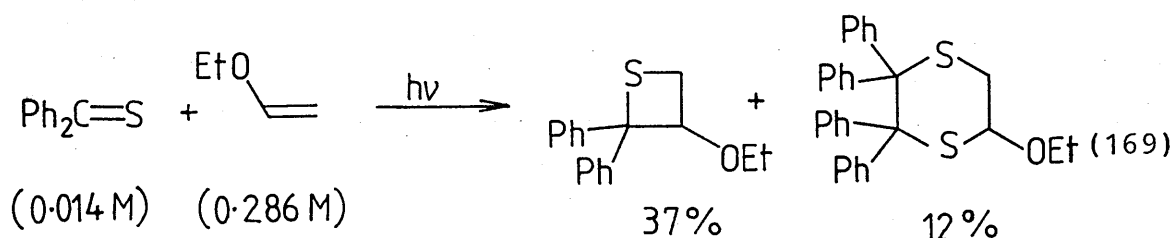


Ethyl vinyl ether leads successfully to thietane products with a variety of other thiocarbonyl compounds, such as adamantanethione⁷⁸, thiobenzophenone¹⁶⁴, and thioparabanates (166)¹⁸². The reactions of the last two, and the regiospecific reaction of the first all take place from the $T(n, \pi^*)$ state; all reactions were carried out in benzene solution, unlike our reaction which was carried out in acetonitrile. In addition the reaction of N-methyldithiosuccinimide with ethyl vinyl ether leads to a regiospecific product (167)¹¹⁰; this too is

in benzene as solvent. The reaction of N-methylphthalimide with ethyl vinyl ether⁴⁶ leads mainly to a ring-expanded benzazepinedione product, but there is probably some oxetane formation which accounts for a methylene product in 7% yield; the regiospecificity is opposite to that observed for the thiocarbonyl compounds (168). It is possible that this reaction occurs from the triplet state, as is the case for other reactions of this type^{42,43}.



The possibility of 2:1 adducts being formed in the reaction of N-methylthiophthalimide and ethyl vinyl ether is supported by a comparison with the thiobenzophenone reaction¹⁶⁴, in which a 1,4-dithiane is seen as a product if high concentrations of thiobenzophenone are employed (169).

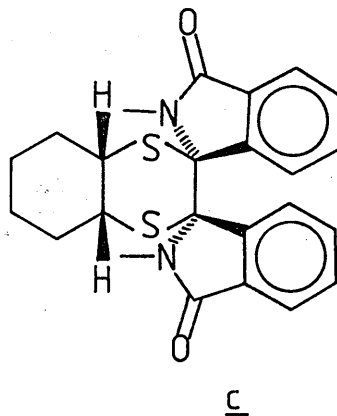
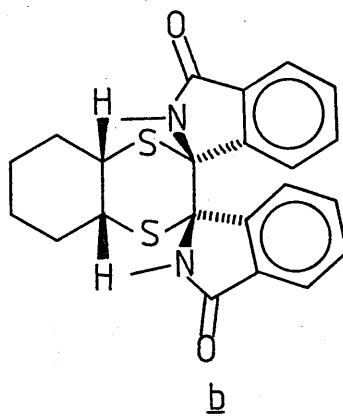
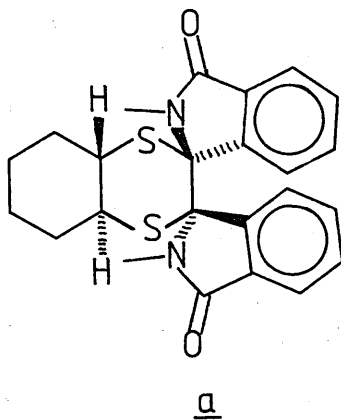


It was decided to explore the possible formation of 2:1 adducts further by irradiating N-methylthiophthalimide in the presence of alkenes which were known to promote 2:1 adduct formation with thiobenzophenone. Those used were cyclohexene and styrene.

The reaction with cyclohexene led to a variety of products in solution, and a precipitated product which was shown by its infrared spectrum to contain a carbonyl group, but the poor quality of the infrared and ¹H-NMR spectra showed that it was a mixture. Separation by column chromatography of the reaction mixture from solution yielded six fractions. The fourth of these was separated further to give one slightly impure product in 4% crude yield. The fifth was also separated further to give a slightly impure product in 16% crude yield, and the sixth was separated to give two rather impure product fractions.

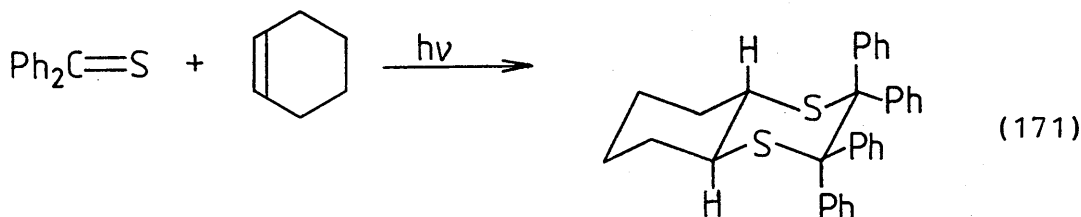
The ¹H- and ¹³C-NMR spectra of the 4% product suggest that it is a 2:1 adduct; the integration in the ¹H-NMR spectrum shows that for one N-methylthiophthalimide molecule (four aromatic protons and a N-CH₃ singlet at δ3.99) there are

approximately half the number of protons required for one cyclohexene molecule (the integration corresponds to six other aliphatic protons - the sample is not completely pure): thus for one cyclohexene molecule in the adduct there are two N-methylthiophthalimide molecules. The chemical shift of the N-CH₃ absorption at δ 3.99 also suggests a 2:1 adduct - see later for styrene experiment - rather than a thietane or dialkylmethylene product, for which the chemical shift might be expected to be in the range 2.8-3.2 ppm. The coincidence of the two N-CH₃ absorptions at δ 3.99 in the ¹H-NMR spectrum, together with their similar values in the ¹³C-NMR spectrum at δ 29.7 and δ 26.5, taken with the appearance of only one carbonyl absorption in the ¹³C-NMR spectrum at 168.2 ppm, and the appearance of only four aliphatic absorptions (of which those at 32.1 and 31.1 ppm are very close) derived from the cyclohexene molecule, would suggest that this 2:1 adduct is close to being symmetrical. Three isomers would seem likely (170a, b and c).



(170)

Any of the above isomers would have to be slightly distorted, in order to account for the non-equivalence of the NCH_3 absorptions in the ^{13}C -NMR spectrum. The cis-fused isomers (170b and c) would seem less likely than the trans-fused isomer (170a); the proposal of a trans-fused structure (170a) is also supported by the ^1H -NMR chemical shifts of the multiplets around $\delta 3.00$, which are consistent with the result for thiobenzophenone^{167,225}, for which the 2:1 adduct is known to have a trans-ring fusion (171), and for which the chemical shift of the ring junction protons is $\delta 3.09$. If the structure is indeed (170a), the chemical shift of the NCH_3 singlet in the ^1H -NMR spectrum, $\delta 3.99$, would suggest that the NCH_3 groups are axial (see later for styrene experiment).

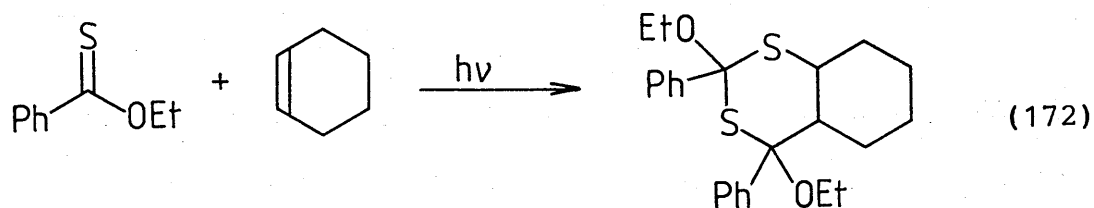


The spectral and analytical data for the crystalline product which was isolated from the fifth fraction in 16% crude yield are consistent with a slightly impure 2:1 adduct. The elemental microanalysis is a close match to that required for a 2:1 adduct, and both the ^1H - and ^{13}C -NMR spectra show appropriate numbers of signals for a 2:1 adduct: the former shows eight aromatic protons, two N-CH_3 singlets at 4.00 ppm and 3.94 ppm and ten other aliphatic protons (the integration for the aliphatic protons is slightly low), whilst the latter shows two carbonyl groups at 169 ppm and 168 ppm, a quaternary carbon absorption at 85 ppm, five cyclohexene-derived absorptions and two NCH_3 absorptions (NCH_3 absorptions at 26.3 ppm and 26.0 ppm). The highest mass peak in the mass

spectrum at 354.046, corresponding to $C_{18}H_{14}N_2O_2S_2$, and the peak at 290.106, corresponding to $C_{18}H_{14}N_2O_2$, would be consistent with two N-methylthiophthalimide moieties (each C_9H_7NOS) linked together.

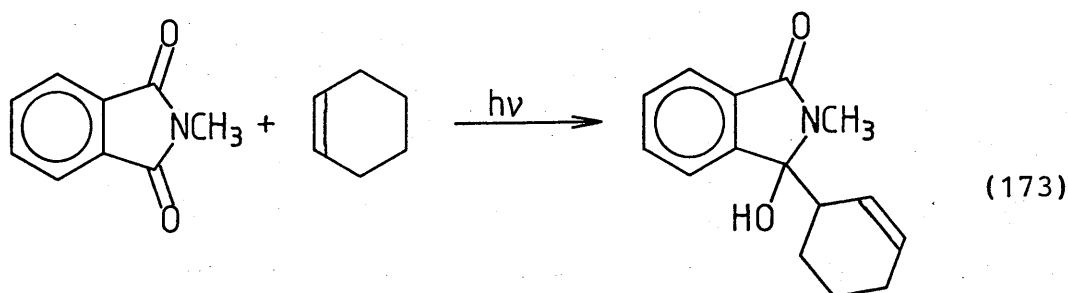
On separation the sixth fraction gave two product mixtures. The first of these shows two singlets at $\delta 2.06$ and $\delta 2.04$ in the 1H -NMR spectrum, and the second, although different overall, also shows these two singlets. These singlets are likely to be derived from NCH_3 protons, and could be indicative of a different 2:1 adduct, by comparison with the products from the styrene experiment (see later).

In previous reports cyclohexene yields either 1:1 or 2:1 adducts with thiocarbonyl compounds, depending on the concentration of the cyclohexene and the substitution pattern around the thiocarbonyl group. O-Ethyl thiobenzoate yields a 2:1 adduct on reaction with cyclohexene (172)¹⁷²; this is, however, a 1,3-dithiane rather than the 1,4-dithiane which is obtained from thiobenzophenone when a low concentration of cyclohexene is used (171)^{167,225}. If a high concentration of cyclohexene is used then the major product is a thietane.



The thiobenzophenone reaction takes place from the (n, π^*) triplet state. There is no competing hydrogen abstraction for the triplet state reaction, although this might occur if the reaction were to take place from S_2 , since the product from the second excited singlet of di-t-butyl thioketone and

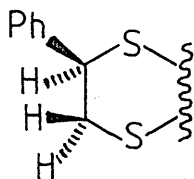
cyclopentene is a hydrogen abstraction product¹⁴². N-Methylphthalimide does not undergo photocycloaddition to cyclohexene, but instead there is a hydrogen abstraction reaction (173). This is because cyclohexene is a 1,2-disubstituted alkene with a relatively low ionization potential, and so electron transfer competes with photocycloaddition⁴⁶.



The other alkene that we used for 2:1 adduct formation with N-methylthiophthalimide was styrene. Column chromatography of the irradiated material gave a series of mixtures, of which two major ones were selected for further purification. The first of these gave a slightly impure 2:1 adduct (4%). Evidence for the adduct involving two molecules of N-methylthiophthalimide and one of styrene comes from the ¹H-NMR spectrum, for which the integration is close to that required for a 2:1 adduct. For thirteen aromatic protons, there are two NCH₃ singlets, at δ 3.65 and δ 3.61, and three other signals, corresponding to a total of three other protons, at δ 4.50, δ 4.03 and δ 3.55. The positions of the NCH₃ singlets at δ 3.65 and δ 3.61 indicate that they do not arise from a spiro-thietane or a methylene product, either of which might be expected to show an absorption in the 2.8–3.2 ppm range. The elemental microanalysis is not completely in agreement with the calculated values for a 2:1 adduct, but nevertheless it is close. The ¹³C-NMR spectrum shows absorptions for two carbonyl groups (δ 169.0 and δ 168.5), a methylene group and a

methine group ($\delta 35.6$ and $\delta 50.0$ respectively) and two NCH_3 carbon atoms ($\delta 29.7$ and $\delta 29.2$). The 1,4-dithiane nature of the product is suggested by the mass spectral fragment at 290, which would indicate a loss of a $\text{S-CHPh-CH}_2\text{-S}$ fragment. Other evidence that this is a 2:1 adduct and not a mixture arises from the melting temperature, which is sharp.

The second fraction from the column also gave an impure 2:1 adduct (14%). Although no satisfactory microanalytical data were obtained, evidence for the presence of a 2:1 adduct comes from the mass spectrum, which shows an ion at 290, which would correspond to loss of $(\text{-SCHPh-CH}_2\text{-S-})$ from a 2:1 adduct. The IR spectrum shows the presence of a carbonyl group at 1696 cm^{-1} ; the $^{13}\text{C-NMR}$ spectrum is also consistent with a 2:1 adduct, showing two carbonyl absorptions at 168.7 ppm and 167.9 ppm, a range of aromatic absorptions, two quaternary carbon absorptions at 81.7 ppm and 80.7 ppm, together with two absorptions at 46.2 and 31.9, arising from incorporation of the styrene moiety into an aliphatic system, and two NCH_3 absorptions at 29.0 ppm and 27.7 ppm. A 90 MHz $^1\text{H-NMR}$ spectrum showed that the compound is slightly impure (the wide melting range would also suggest this to be the case), and it was not possible to observe the ABX pattern which might be expected for the three protons from the styrene moiety. However the higher resolution afforded by a 400 MHz spectrum clearly demonstrates this pattern, with H_X at $\delta 4.73$ showing couplings of 11 Hz and 9 Hz to H_A and H_B respectively (J_{AX} is expected to be larger than J_{BX} because H_A and H_X are diaxial) and H_A at $\delta 4.00$ appearing as a slightly distorted triplet on account of J_{AX} (11 Hz) and J_{AB} (12 Hz) being close in value. H_B , at $\delta 3.89$, shows couplings J_{AB} (12 Hz) and J_{BX} (9 Hz).



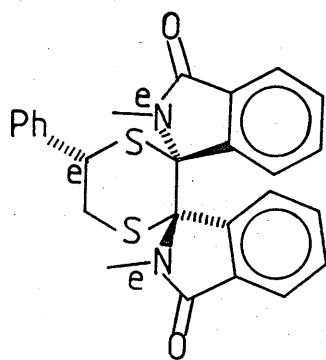
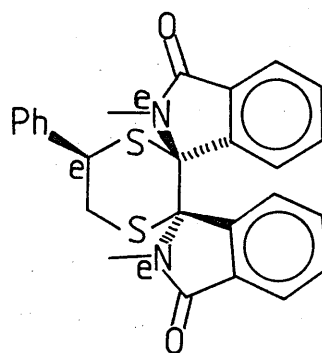
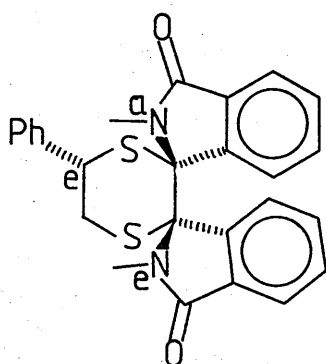
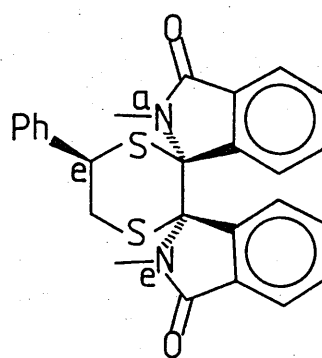
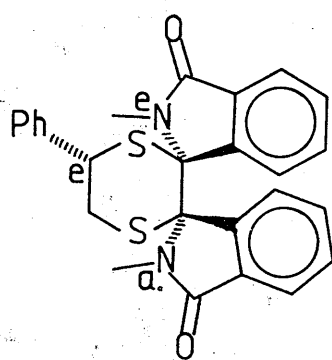
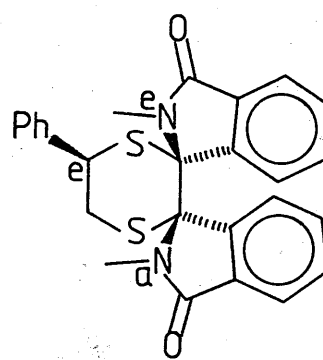
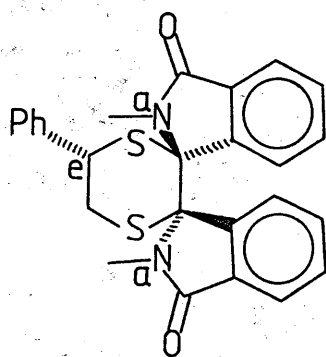
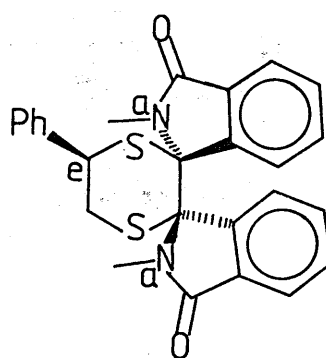
(174)

The ^1H -NMR spectrum also shows aromatic protons (the integration is higher than the expected value of thirteen, probably due to the presence of impurities), and two NCH_3 singlets at $\delta 2.17$ and $\delta 2.05$.

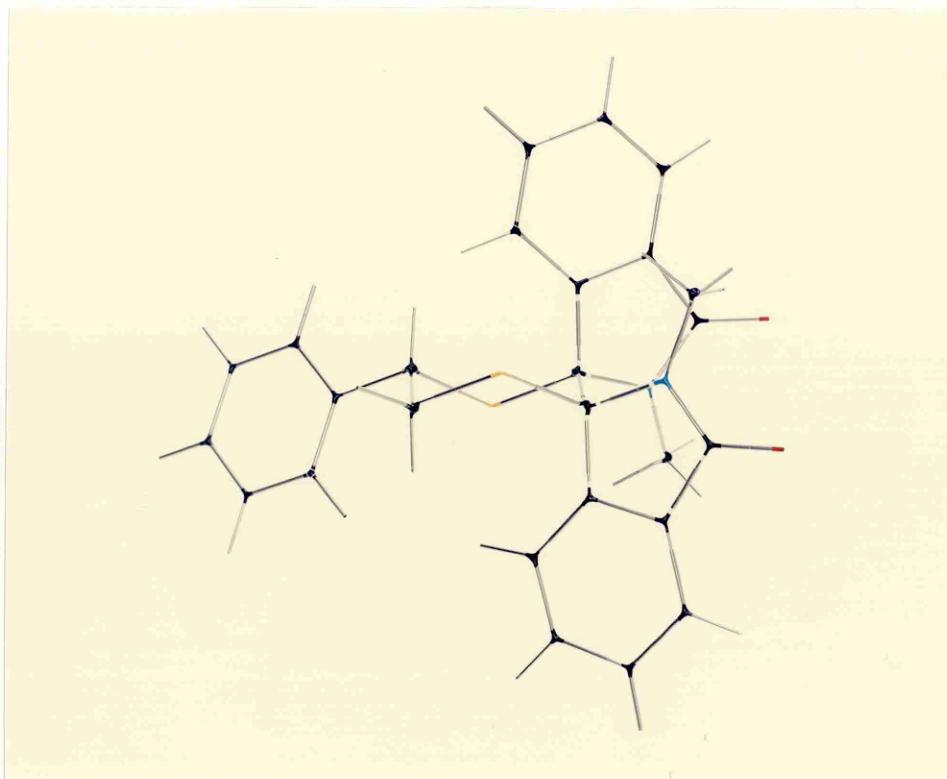
At this point it is appropriate to discuss the stereochemistry of the 2:1 adducts. Eight possible isomers may be formed: these are four mirror-image pairs (175).

The 1,4-dithiane ring is assumed to be in the chair conformation and the phenyl group has been assumed to be equatorial in each case, as it is a large substituent, and the 'a' or 'e' at a spiro-junction refers to the NCH_3 group, which appears from models to be the bulkier substituent of the isoindolinone moiety. Drieding models of four isomers were made and photographed: photograph 1 corresponds to structure a, photograph 2 to structure c, photograph 3 to structure f and photograph 4 to structure h.

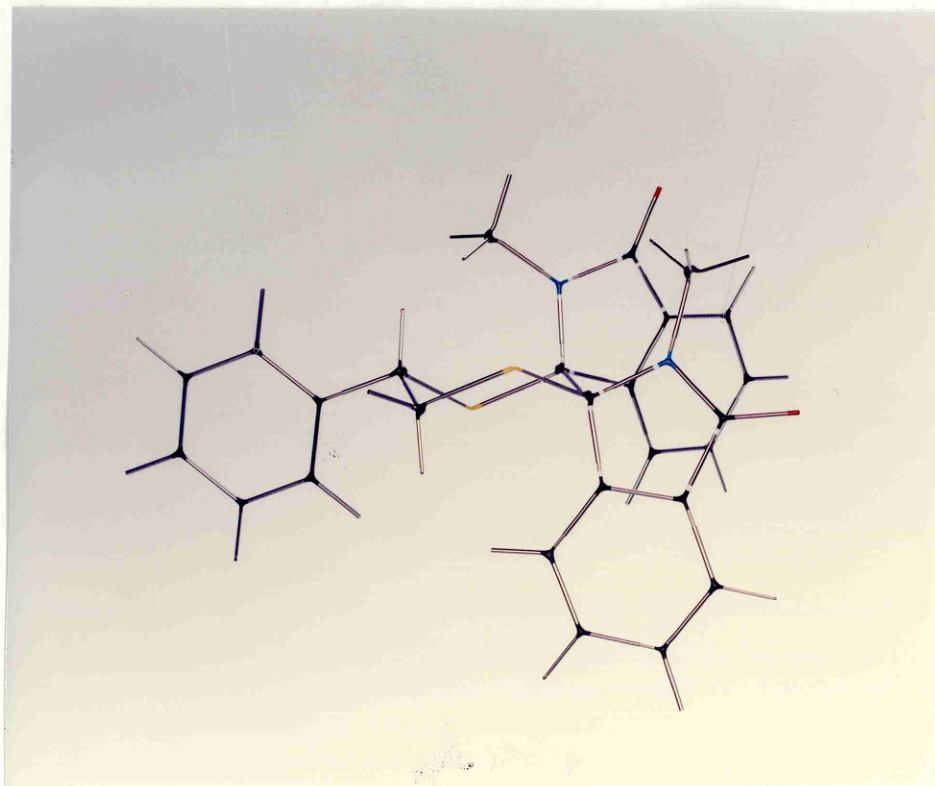
Photograph 1 shows that the configuration with both NMe groups equatorial appears to be the least sterically crowded. It also shows that the NCH_3 groups approach close to, and above, the aromatic rings of the adjacent spiro-group. The ring current might be expected to show a shielding effect, thus causing both NCH_3 groups to exhibit similar, low chemical shifts. It is likely that the 2:1 adducts which show both NCH_3 groups close to $\delta 2.0$ have this stereochemistry. Photograph 4 shows that the configuration in which both NCH_3 groups are

abcdefgh

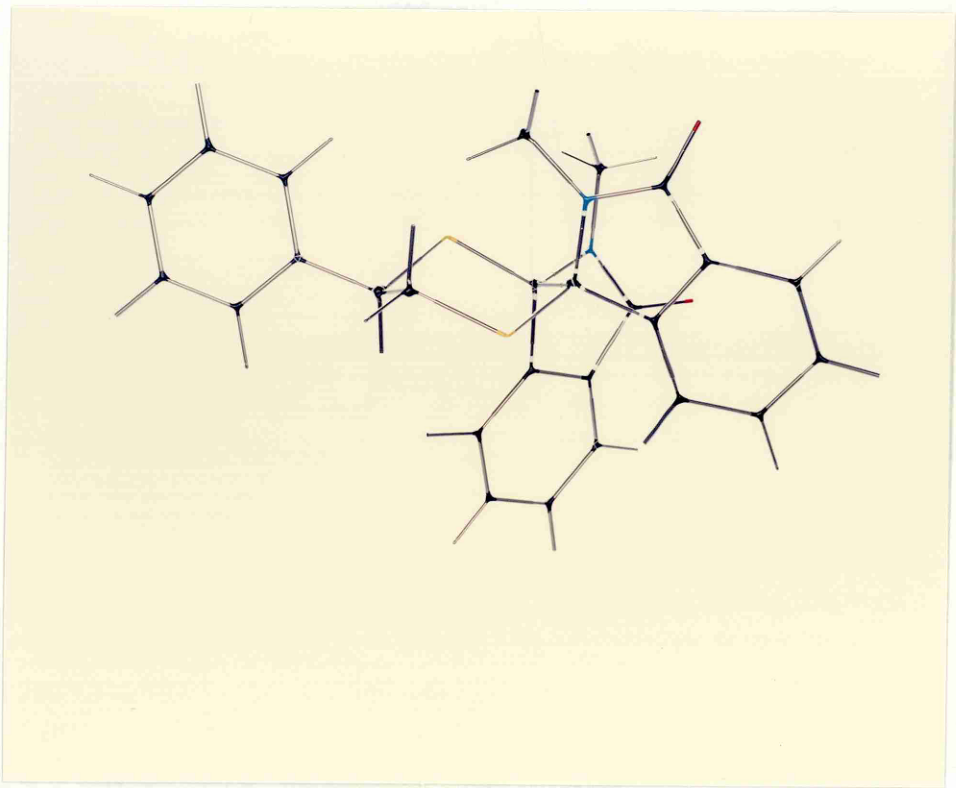
(175)



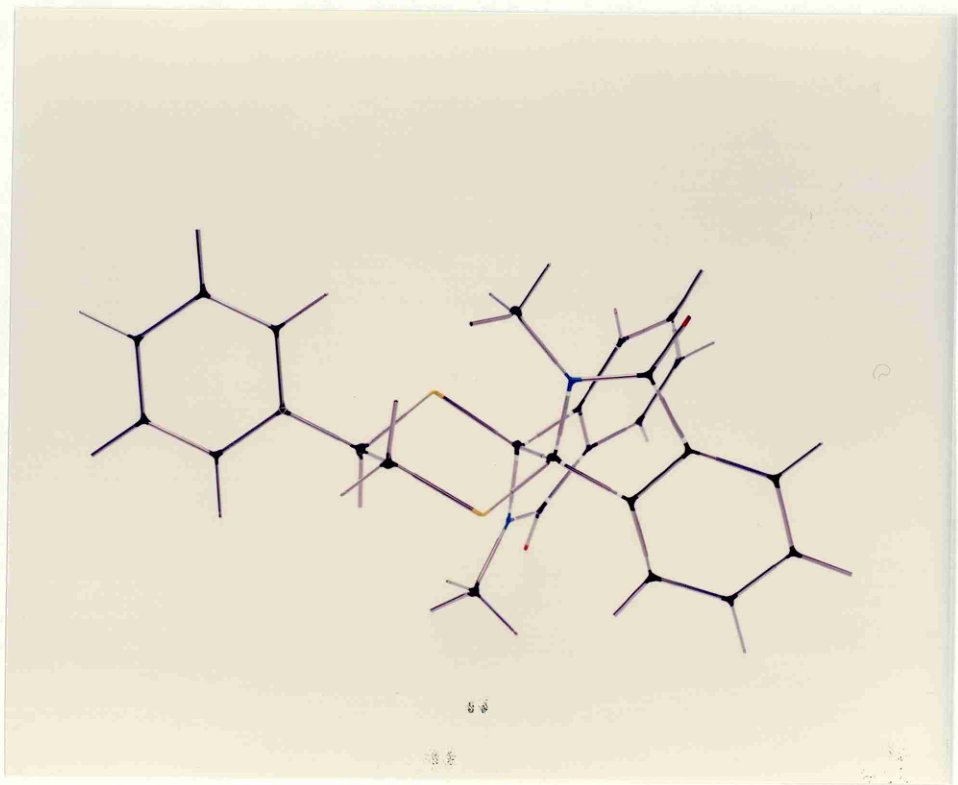
Photograph 1



Photograph 2



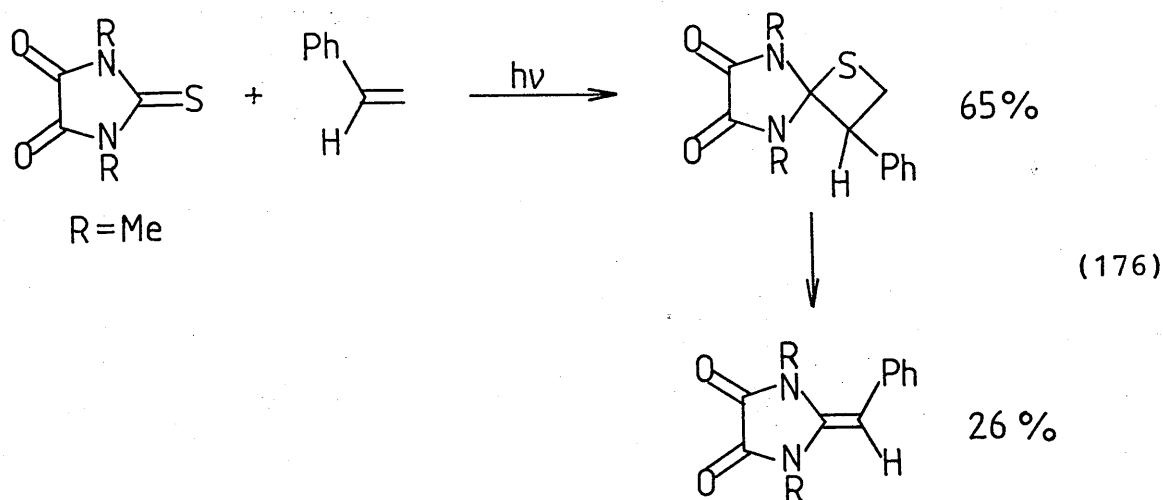
Photograph 3



Photograph 4

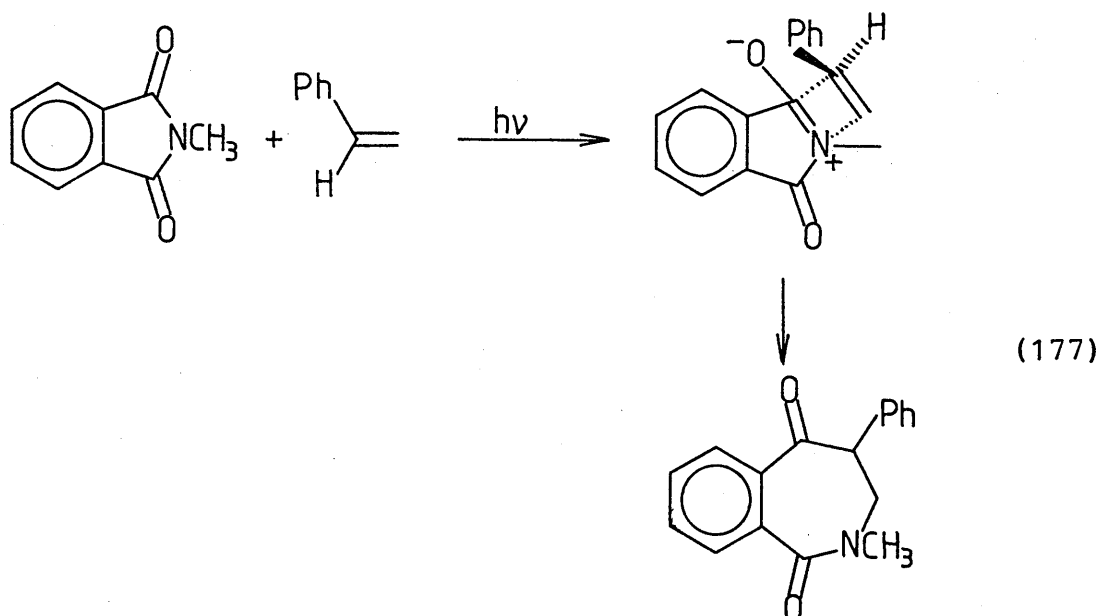
axial is sterically rather crowded; both NCH_3 groups are over the dithiane ring and in the region of the lone pairs of the sulphur atoms. The two groups of NCH_3 protons might be expected to be somewhat deshielded, but in similar environments, and it is likely that the 2:1 adducts which show both NCH_3 groups close to $\delta 4.0$ have this stereochemistry. It would not be possible to make reliable predictions concerning the chemical shifts of the NCH_3 groups for the configurations in which one NCH_3 group is axial and the other is equatorial (photographs 2 and 3).

Previously reported reactions between thiocarbonyl compounds and styrene proceed from the $\text{T}(\text{n}, \pi^*)$ state and lead regiospecifically to thietanes in the case of xanthione¹⁶⁴, thioparabanates (176)¹⁸² and thiobenzophenone^{167,225}; in the case of thiobenzophenone the 1,4-dithiane is an additional product, isolated under similar conditions to those for cyclohexene.



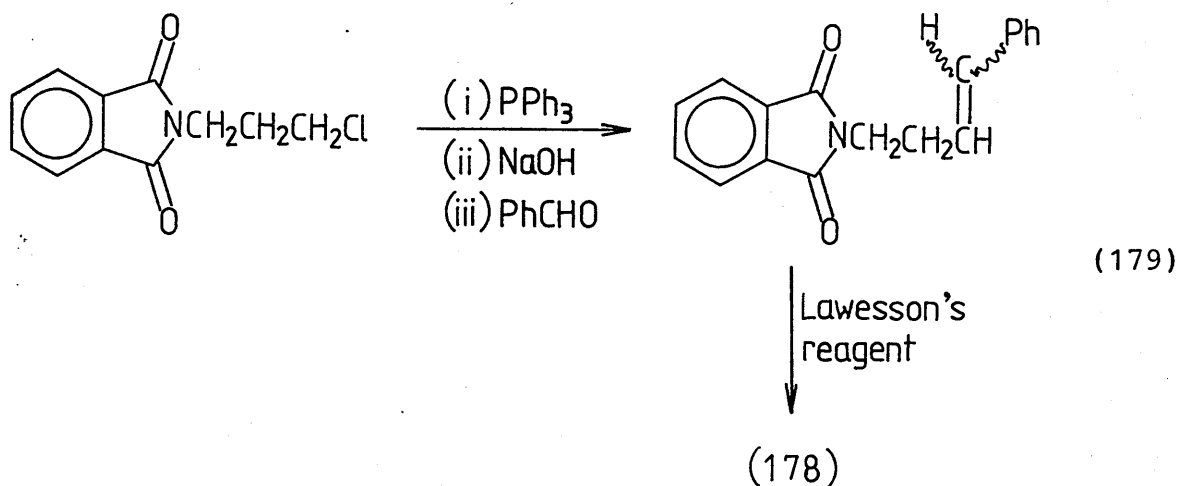
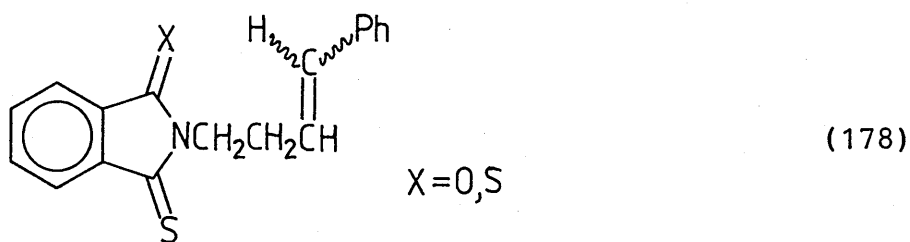
Irradiation of N-methylphthalimide in the presence of styrene leads (in the absence of an alcoholic solvent) mainly to a benzazepinedione (177)^{50(b)}. The regiospecificity in the product is due to the orientation of the styrene moiety in the

intermediate exciplex⁴⁸. In the case of α -methylstyrene there is a competing intersystem crossing which results in the formation of oxetane products as well as the benzazepinedione⁴².



We conclude that N-methylthiophthalimide is capable of giving both thietane and 1,4-dithiane products with alkenes, in much the same way as for other thiocarbonyl compounds, and in contrast to related imides.

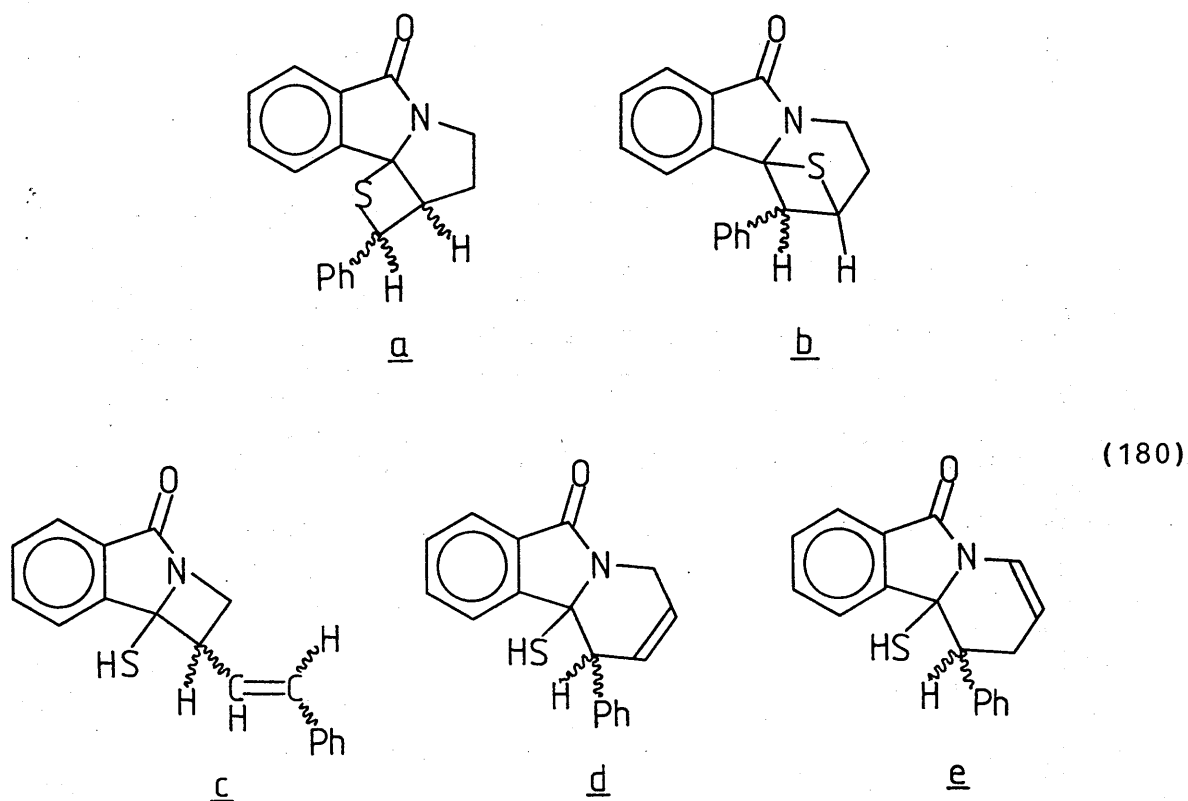
In view of the successful intramolecular photoreactions reported for N-alkenyl phthalimides, we prepared and irradiated the N-(4-phenylbut-3-enyl)thiophthalimides (178). The starting materials were prepared by thiation of the corresponding N-substituted phthalimide using Lawesson's reagent. N-(4-Phenylbut-3-enyl)phthalimide was prepared via a Wittig reaction using N-(3-chloropropyl)phthalimide for reaction with triphenylphosphine, and benzaldehyde as the carbonyl component of the reaction (179).



Irradiation of a mixture of cis- and trans-N-(4-phenylbut-3-enyl)thiophthalimide led to the formation of one major product. Elemental microanalysis showed this product to have the same empirical formula as the starting material, and the mass spectrum also showed a parent ion peak at 293. Both the ^{13}C -NMR and infrared spectra indicated the presence of a carbonyl group in a five-membered lactam ring; the ^{13}C -NMR spectrum also showed that no thiocarbonyl group was present. The infrared spectrum showed a signal at 2527 cm^{-1} , which may be attributed to S-H stretching, and the singlet at $\delta 2.05$ in the ^1H -NMR spectrum was also suggestive of an O-H, N-H or S-H proton. Both the ^{13}C - and ^1H -NMR spectra suggested the presence of a $-\text{CH}=\text{CH}-$ bond ($\delta 6.10$ (m, H) and $\delta 5.85$ (m, 1H) in the ^1H -NMR spectrum, and more absorptions in the unsaturated/aromatic region of the ^{13}C -NMR spectrum than could be accounted for by a single aromatic ring). Taking these factors into

account, both of the possible thietanes (180a and b) may be discounted on the basis that no $-\text{CH}=\text{CH}-$ bonds are present.

By contrast, thiol products (180c, d and e) seem more likely on the basis of the infrared and ^1H -NMR spectral data, and are supported by the appearance of three saturated aliphatic signals in the ^{13}C -NMR spectrum, one of which, at $\delta 69.4$ is from a quaternary carbon atom.



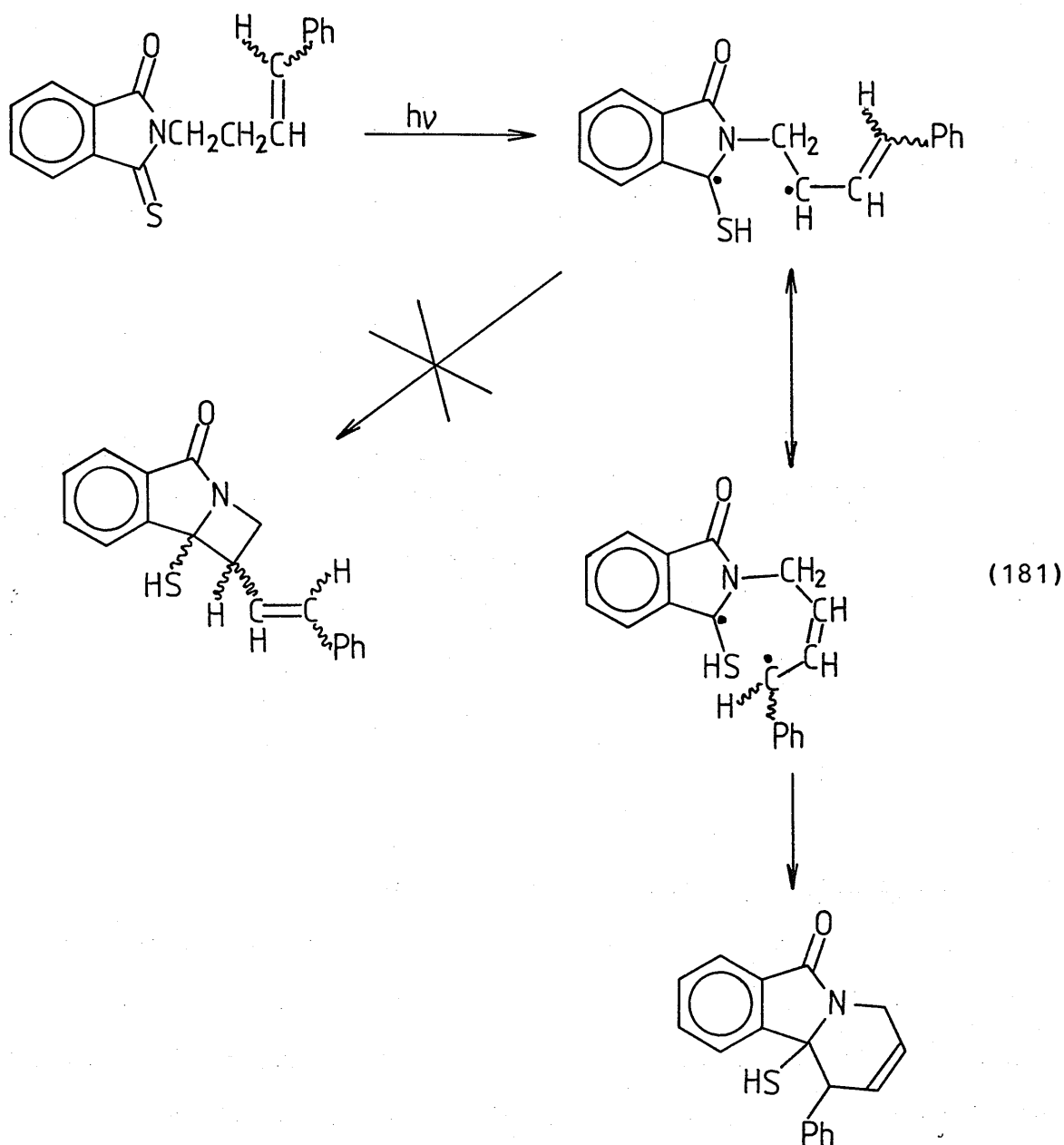
The extent of the proton coupling in the ^1H -NMR spectra, which was shown by decoupling experiments, and the double bond coupling of 10.1 Hz, indicating a cis-double bond, serve to indicate that the non-aromatic protons (bar the $-\text{SH}$ proton) are part of a cyclic structure, and thus thiols (180d and e) are more likely than thiol (180c). The proton coupling patterns are shown in Table 2.1.

Chemical shift	δ 5.86	δ 4.80	δ 3.99	δ 3.65
δ 6.10	10.1	3.3	4.4	3.9
δ 5.86	-	2.4	2.4	2.4
δ 4.80	-	-	(-) 18.7	3.4
δ 3.99	-	-	-	2.3

Table 2.1 Coupling constants (Hz) observed in the ^1H -NMR spectrum of the thiol product

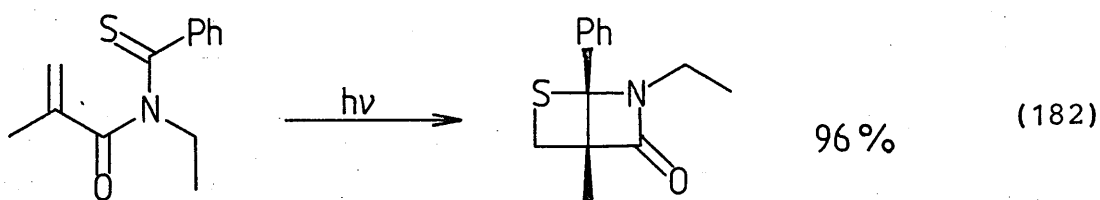
Structure (180d) seems to be more likely than structure (180e) on the grounds of the chemical shifts of the methylene and methine positions in the ^1H -NMR and ^{13}C -NMR spectra. A chemical shift of 37.8 ppm (slightly higher than the N-methylthiophthalimide NCH_3 value) seems consistent with the methylene group in (180d), but is high for that in (180e); this is also reflected by the ^1H -NMR chemical shifts for the methylene protons. It would also be expected that if the double bond were adjacent to a nitrogen atom there would be more than 0.24 ppm difference between the two olefinic protons in the ^1H -NMR spectrum.

The occurrence of hydrogen abstraction rather than photocycloaddition is surprising and may be due to geometric considerations. Both of the possible thietane products (180a and b) are highly geometrically strained, and thus would not be expected to form easily. By contrast, the thiol product (180d) is relatively unstrained, and might be expected to be formed more easily; a possible mechanism for the reaction is given below (181).

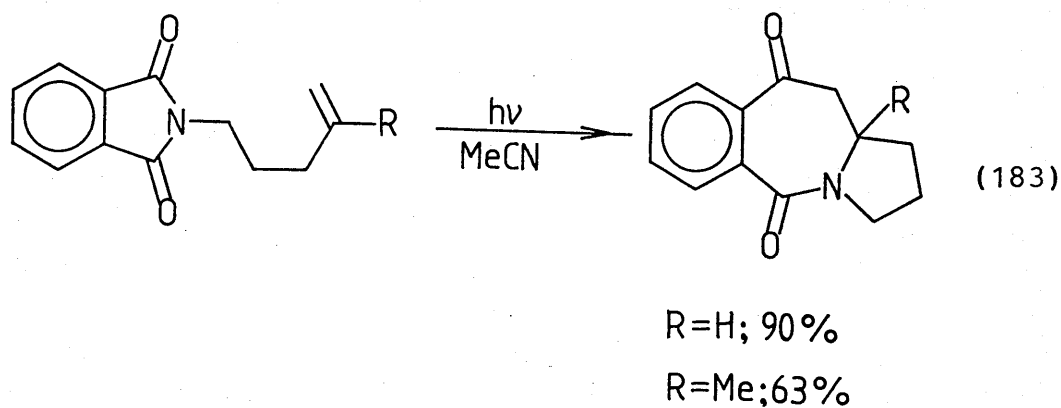


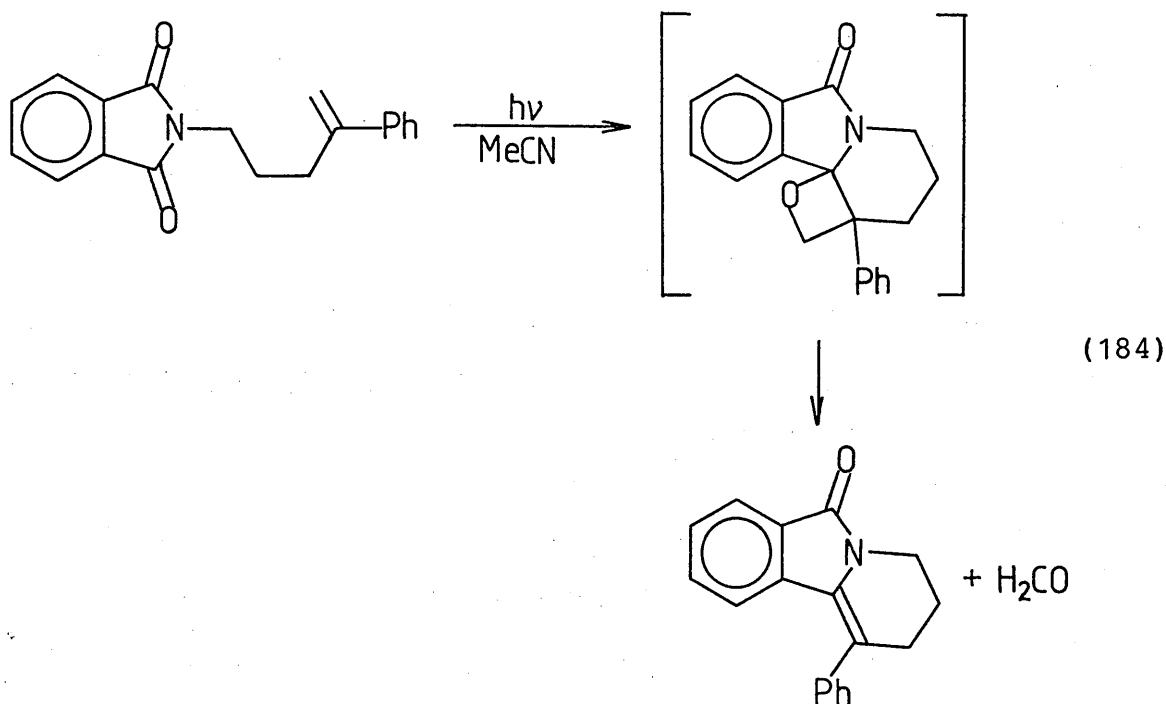
Irradiation of a mixture of cis- and trans-N-(4-phenylbut-3-enyl)dithiophthalimides appeared to give only oxidation products. All product fractions showed carbonyl absorptions in their infrared spectra.

Only one other example of an intramolecular photocycloaddition of a thioimide is known; this is a preparation of a β -lactam from an acyclic, α,β -unsaturated system (182)¹⁸¹.



For phthalimides, intramolecular alkene reactions have been more widely investigated. N-Pent-4-enylphthalimides (183) yield benzazepinedione products following irradiation in acetonitrile⁴⁸. However, most of the reactions have been carried out in alcohol solution, resulting in the formation of solvent-incorporated products⁵⁴. The analogous phenyl-substituted compound reacts very slowly (via the triplet state) to yield a product derived via an oxetane (184)⁴²; it is not clear why this electron-rich alkene does not react by electron transfer.





We irradiated two electron-deficient alkenes in excess with N-methylthiophthalimide. The irradiation with acrylonitrile ($\text{CH}_2=\text{CH}-\text{CN}$) led to a low yield of isolated products. However, there may have been some more low R_f products as the weight of the fractions from the chromatography column does not account for all of the N-methylthiophthalimide which was consumed in the reaction.

The reaction of N-methylthiophthalimide with methyl acrylate ($\text{CH}_2=\text{CH}-\text{COOMe}$) was carried out twice. The first reaction gave 81% conversion of N-methylthiophthalimide in fifty hours. The reaction mixture was separated by column chromatography to yield several mixed fractions, of which the fourth to ninth inclusive were product fractions, and appeared by their ^1H - and ^{13}C -NMR spectra to be of interest; these were separately recrystallised.

The fourth fraction could not be purified, but the spectral evidence indicated that it may have contained a thietane product; the ^1H -NMR spectrum showed singlets between $\delta 3.4$ - 2.8 ,

which may arise from NCH_3 or COOCH_3 protons, and would be in keeping with the NCH_3 shift values of around $\delta 3.1$ - 2.8 observed in previous thietanes.

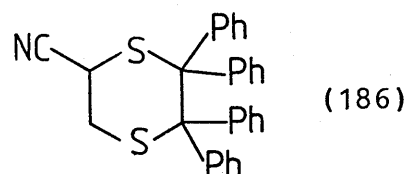
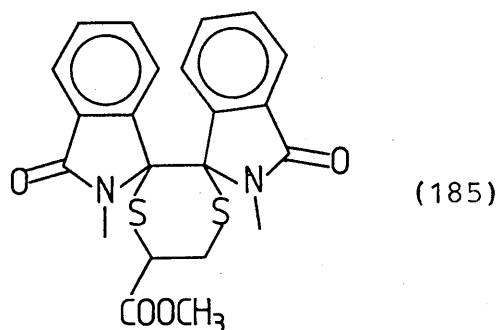
The recrystallised product from the fifth fraction showed an integration in the ^1H -NMR spectrum which was more consistent with a 1:1 than a 2:1 adduct, and a doublet of doublets at $\delta 5.20$, which would be consistent with a thietane methine proton.

The recrystallised product from the sixth fraction appeared to be a 2:1 adduct; supporting evidence came from the microanalysis, for which the values were close to the calculated values for a 2:1 adduct. The ^1H -NMR spectrum showed an integration which is appropriate for a 2:1 adduct: eight aromatic protons, three singlets of three protons each (two NCH_3 and one COOCH_3) and a total of three other aliphatic protons. The ^{13}C -NMR spectrum showed two carbonyl absorptions, and the indication that this was not a mixture came from the sharp melting temperature.

The seventh and eighth fractions could not be purified, but the ninth fraction was recrystallised to give a different 2:1 adduct: the ^1H -NMR spectrum showed eight aromatic protons, three singlets of three protons each, and a total of four other aliphatic protons (this compound is not completely pure). The ^{13}C -NMR spectrum showed five aliphatic absorptions, which would account for two NCH_3 and a $\text{CH}_3\text{OOC}-\overset{|}{\text{CH}}-\overset{|}{\text{CH}_2}$ moiety. The sharp melting temperature indicated that the product was not a mixture, and the microanalysis result was close to the calculated values for a 2:1 adduct. The mass spectrum showed a mass ion at 290, which would be consistent with loss of $-\text{S}-\text{CH}-\text{CH}_2-\text{S}-$ from a 2:1 adduct.

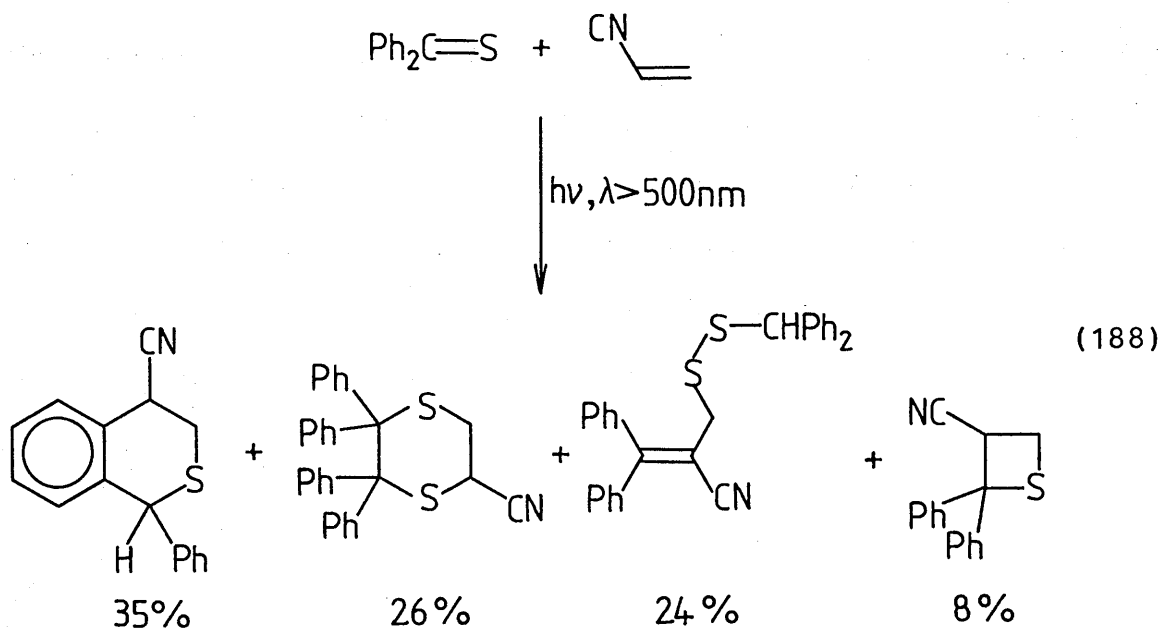
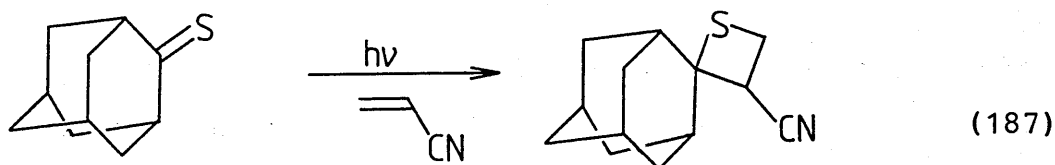
$$\begin{array}{c} | \\ \text{COOCH}_3 \end{array}$$

Both of the 2:1 adducts showed a fragment $C_{18}H_{14}N_2O_2$ in their mass spectra: this suggests that the adducts are 1,4-dithianes (185). Although the 1H -NMR chemical shifts are not available for an analogous 1,4-dithiane, those of 5-cyano-2,2,3,3-tetraphenyl-1,4-dithiane (186)¹⁷⁴ provide a useful comparison. In this dithiane the methine proton is at $\delta 4.18$; our first 2:1 adduct shows a multiplet at $\delta 4.40$ and a doublet at $\delta 4.20$, and the second a multiplet at $\delta 4.40$. For the dithiane (186) the methylene protons give rise to a multiplet at $\delta 3.60$ - 3.00 ; our first 2:1 adduct shows a multiplet at $\delta 3.40$, and the second a multiplet at $\delta 3.20$. It is not possible to assign the stereochemistry of these 2:1 adducts, as there is no way of distinguishing between the ester methyl group and the N-methyl groups.



The experiment with methyl acrylate was repeated with a methyl acrylate: N-methylthiophthalimide ratio of 1:3, and the reaction mixture was maintained at about $-30^\circ C$ in order to inhibit evaporation of the methyl acrylate. The reaction was stopped after fifty-five-and-a-half hours. 1H -NMR and infrared analysis of the product mixture showed it to contain very little other than N-methylthiophthalimide and its oxidation product N-methylphthalimide. It is possible that the lack of reaction may be attributed to the low concentration of the alkene.

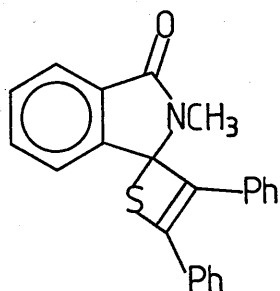
The photoreactions of other thiocarbonyl compounds with electron-deficient alkenes produce a range of products. Reaction occurs either from the $S_2(\pi, \pi^*)$ state, in which case only thietane products are isolated, as for acrylonitrile²²⁶ with thiobenzophenone or methyl acrylate with xanthione¹⁷⁵; or reaction occurs from the $T_1(n, \pi^*)$ state, in which case a variety of products may be formed. The thietane product is formed regiospecifically in the reactions of methyl acrylate with thioparabanates¹⁸², or of acrylonitrile with adamantanethione (187)⁷⁸, and non-stereospecifically in the reactions of fumaronitrile or maleonitrile with xanthione¹⁷⁵. When thiobenzophenone is irradiated at long wavelengths in the presence of acrylonitrile four products are obtained (188)¹⁷⁴. A benzo-thiapyran product is obtained, in similar yield to the thietane, in the irradiation of thiobenzophenone with methyl acrylate¹⁶⁴. N-Methylphthalimide does not give products when irradiated in the presence of ethyl acrylate or acrylonitrile⁴⁶.



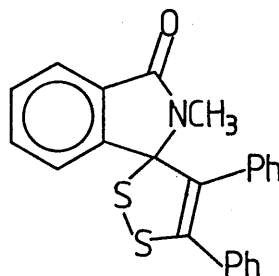
Thus the overall picture which emerges from the results of these reactions with alkenes is that the N-methylthiophthalimides react only at the thiocarbonyl group (possible reasons for this will be discussed in the following chapter), to form mainly thietanes or 1,4-dithianes. The reaction is regioselective as shown by the reaction between 1,1-diphenylethene and N-methylthiophthalimide, and non-stereospecific, as shown by the reaction between cis-stilbene and N-methylthiophthalimide. There is no evidence for the formation of analogues of benzazepinediones, and in this respect the N-methylthiophthalimides do not resemble N-methylphthalimide. However, the thietanes and 1,4-dithianes formed in the reactions are analogous to the products formed in photocycloaddition reactions of alkenes with thioketones.

To extend our understanding of the scope of the photocycloaddition reactions of the N-methylthiophthalimides, we have used a variety of other addends with multiple bonds. First a range of alkynes was studied, including both electron-donor and electron-acceptor substituted alkynes.

Irradiation of N-methylthiophthalimide with diphenylethyne gave a spirothiete product (189). A second, green product was also isolated in low yield from the work-up of the reaction mixture, and was assigned the spiro-1,2-dithiole structure (190).

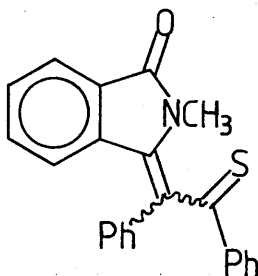


(189)



(190)

The structure of the spirothiete was established on the basis of the mass spectrum (parent ion at 355.103 corresponds to a 1:1 adduct) and elemental microanalysis (results consistent with a 1:1 adduct); the ^1H -NMR spectrum, which showed only fourteen aromatic protons and an NCH_3 group; the infrared spectrum, which indicated a five-membered lactam carbonyl group; and the ^{13}C -NMR spectrum which showed an amide carbonyl group (168.1 ppm), a quaternary aliphatic carbon atom (78.0 ppm), and alkene and aromatic carbons. The lack of thiocarbonyl absorption and the presence of a quaternary aliphatic carbon in the ^{13}C -NMR spectrum indicated that the structure was as shown above, and not the isomeric ring-opened unsaturated thioketone (191) which might be expected by comparison with the photoreactions of ketones with alkynes, in which oxetes are not isolated. In order to determine whether a reversible ring-opening reaction might occur in solution, a ^1H -NMR spectrum was taken at 323 K and compared with that run at 300 K: no difference was seen, indicating that ring-opening, which would be expected to alter the NCH_3 chemical shift and the aromatic absorption pattern, does not occur to any significant extent. However, the temperature range studied was very limited.



(191)

The spiro-1,2-dithiole structure (190) is assigned on the basis of microanalytical ($\text{C}_{23}\text{H}_{17}\text{NOS}_2$) and mass spectral (parent ion at 387.076) data; the infrared spectrum shows a five-membered lactam carbonyl group. As the quantity of this

product was small a full spectral characterisation could not be carried out. However, another basis for proposing that the structure is (190) is that in the reaction of diphenylethyne with dimethylthioparabanate both a spirothiete and a spiro-dithiole are formed²⁰².

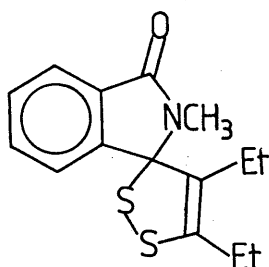
To see whether the dithiole product is present in the initial product mixture, the reaction between N-methylthiophthalimide and diphenylethyne was repeated, and the crude reaction mixture was analysed by ¹H-NMR and infrared spectra. These showed that all bar one of the strong and medium absorptions in the infrared spectrum and all of the absorptions observed in the ¹H-NMR spectrum could be accounted for by N-methylthiophthalimide and the spirothiete product. We therefore can say that (190) is not formed in anything other than very small quantities in the photoreaction, and it may be produced during the work-up procedure.

In the irradiation of N-methyldithiophthalimide with diphenylethyne the N-methyldithiophthalimide was recovered almost quantitatively; small quantities of polar products (methanol was needed to elute them from a silica column) were obtained, and infrared spectra of these showed them to be oxidation products.

N-Methylthiophthalimide was irradiated in the presence of phenylethyne. This reaction was carried out twice; no products appeared to be formed, but this is possibly because of the short reaction times used: one and six hours respectively, compared with a reaction time for diphenylethyne of twenty-two hours. It would be interesting to repeat this experiment using a longer irradiation time.

N-Methyldithiophthalimide was also irradiated with phenylethyne. Infrared and ^1H -NMR spectra of the reaction mixture suggested that the main reaction which was taking place was oxidation.

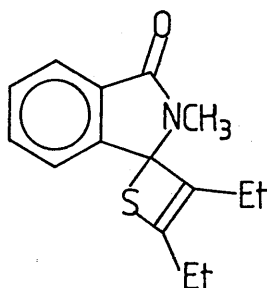
As an example of an alkyl- rather than an aryl-substituted alkyne, hex-3-yne was irradiated with N-methylthiophthalimide. Two products were obtained, the first of which was 4',5'-diethyl-2-methyl-2,3-dihydro-1H-isoindole-3-spiro-3'-1',2'-dithiol-1-one (192), in 5% yield. The microanalysis results were consistent with the dithiole structure, and the mass spectrum showed a parent ion for $\text{C}_{15}\text{H}_{17}\text{NOS}_2$. The infrared spectrum showed an absorption at 1703 cm^{-1} , indicating a carbonyl group in a five-membered lactam ring. Both the ^{13}C - and ^1H -NMR spectra showed two ethyl groups, one NCH_3 group and one disubstituted aromatic ring. To observe the quaternary carbon signals it would be necessary to run the ^{13}C -NMR spectrum again using a relaxation reagent such as $\text{Cr}(\text{acac})_3$.



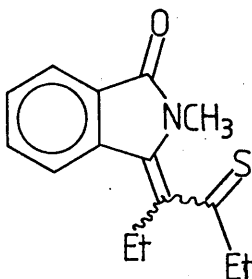
(192)

The second, and slightly impure, product was the major product (40% crude yield): 3',4'-diethyl-2-methyl-2,3-dihydro-1H-isoindole-3-spiro-2'-thiet-1-one (193). The mass spectrum showed the highest mass ion at 259, which would be consistent with the parent ion of a 1:1 N-methylthiophthalimide: hex-3-yne adduct. The ^1H -NMR spectrum was similar to that of the dithiole product, but with the ethyl groups shifted a little, and the infrared spectrum showed an absorption at 1714 cm^{-1} , which

indicated a carbonyl group in a five-membered lactam ring. The ^{13}C -NMR spectrum was consistent with the spiro-thiete structure, showing a carbonyl group, an aromatic ring and five aliphatic carbon atoms; no quaternary aliphatic carbon signal is observed, but it is possible that this is obscured by the chloroform absorptions. The ^{13}C -NMR spectrum showed no thio-carbonyl group, and so the possible unsaturated thioketone structure (194) was ruled out.



(193)

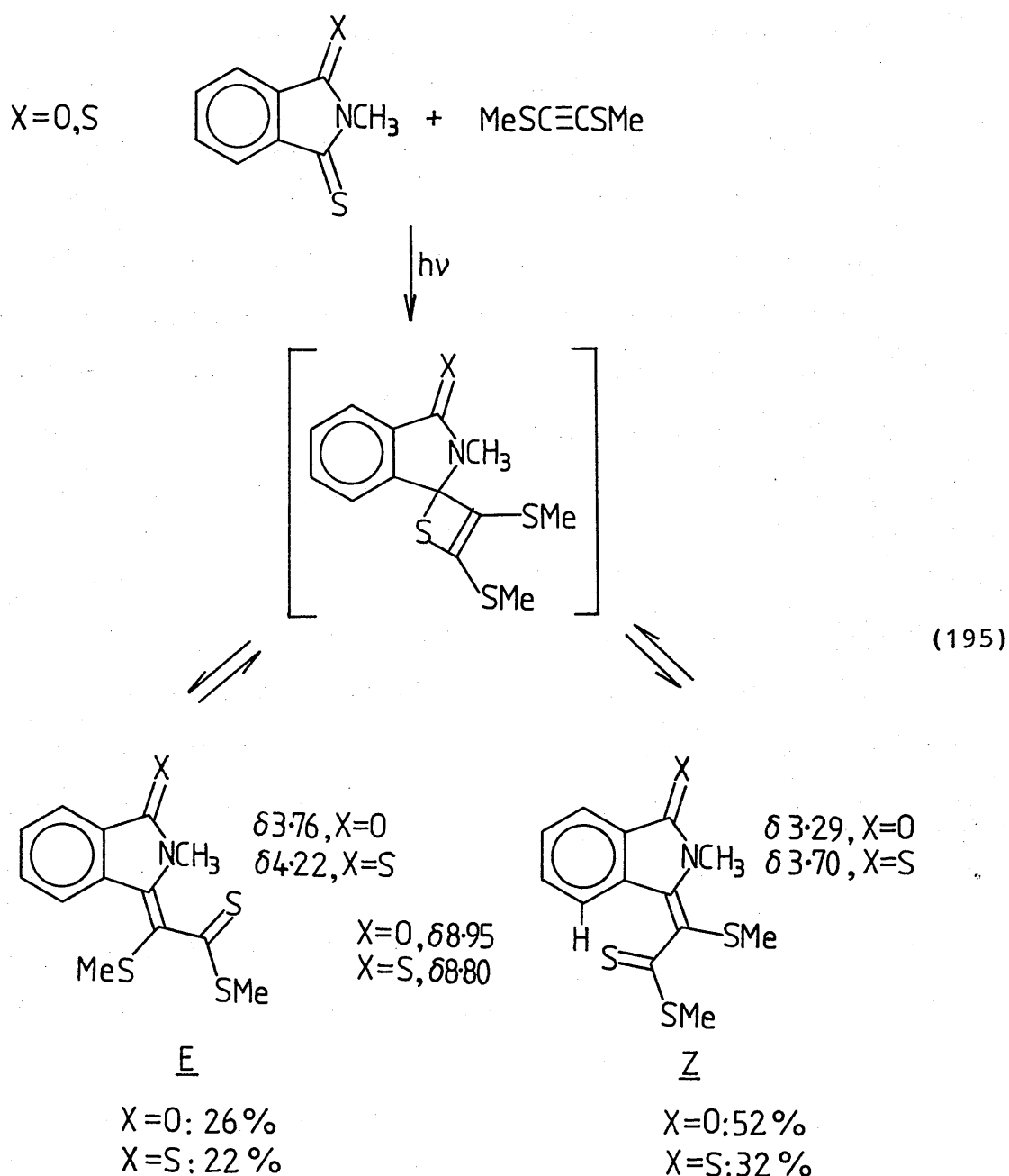


(194)

N-Methyldithiophthalimide was also irradiated with hex-3-yne; much of the N-methyldithiophthalimide was recovered unreacted, and the products which were obtained were shown by their infrared spectra to be oxidation products.

The electron-deficient alkyne dimethyl acetylenedicarboxylate was irradiated with N-methyldithiophthalimide. The infrared and ^1H -NMR spectra of the crude reaction mixture suggested that some products other than oxidation products had been formed, but the mixture was not separated.

The success of the reactions between aryl- or alkyl-thioketones and alkylthioethynes^{203-5,207}, reported by Professor Bos' group, led to our collaboration with them to investigate the reactions between bis(alkylthio)ethynes and the N-methylthiophthalimides. Irradiations of the N-methylthiophthalimides with bis(methylthio)ethyne led to mixtures of E- and Z- α,β -unsaturated dithioesters (195).



The microanalysis values from the crystalline product were consistent with a 1:1 adduct, and the mass spectrum also showed the highest mass ion at 295, which would be the $C_{13}H_{13}NOS_3$ parent ion. The infrared spectrum showed a carbonyl absorption at 1715 cm^{-1} , which would be appropriate for a carbonyl group in a five-membered lactam ring. Although the crystalline form of the product appears to contain only one component, as indicated by the sharpness of the melting temperature, a solution is shown by both ^1H - and ^{13}C -NMR to contain both E- and Z-unsaturated dithioesters.

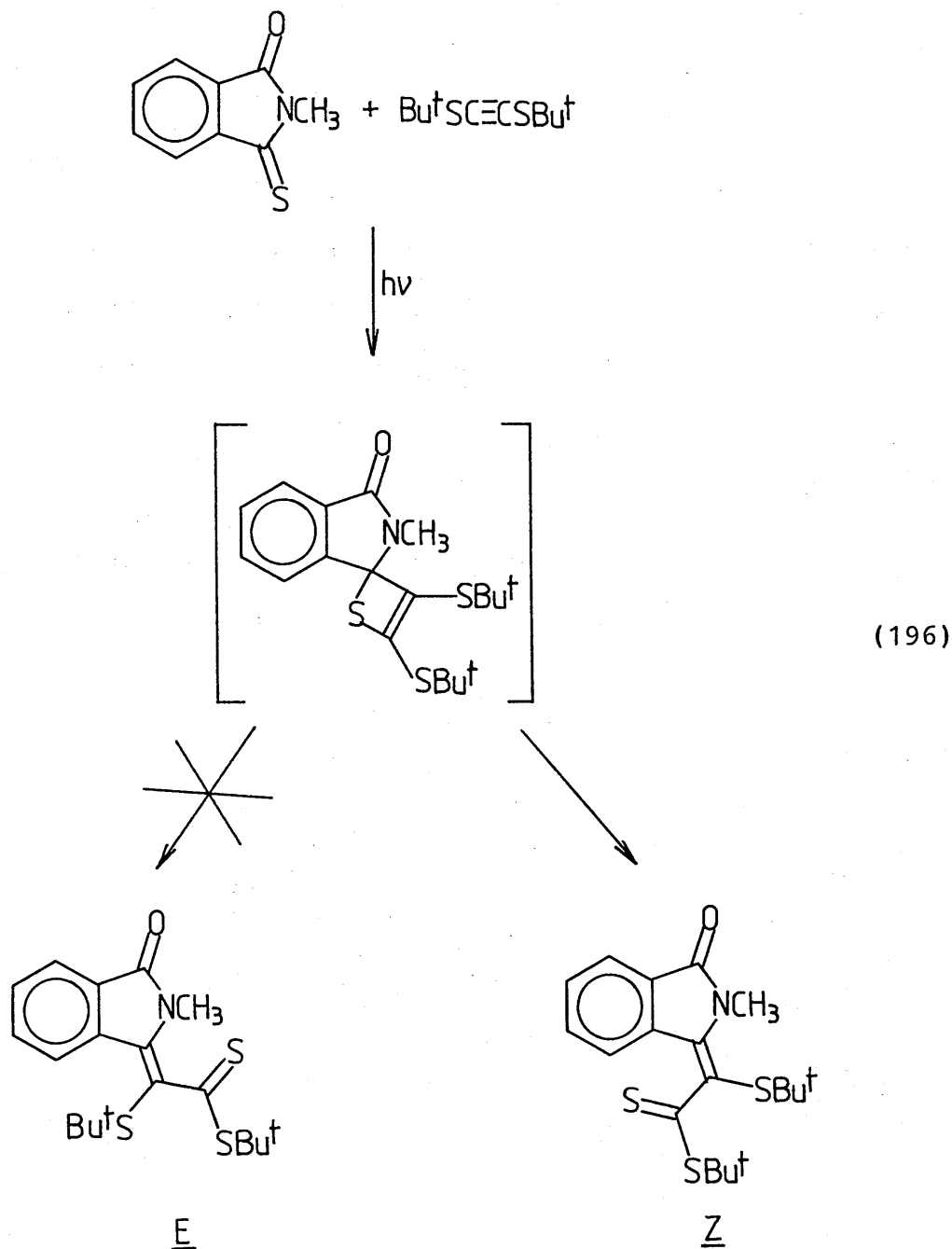
The isomer ratios are obtained from the ^1H -NMR spectra. The assignment of the Z- α,β -unsaturated dithioester as major and the E-compound as minor is also made on the basis of the ^1H -NMR spectra. The NCH_3 protons are more highly deshielded ($\delta 3.76$ for $X = \text{O}$, $\delta 4.22$ for $X = \text{S}$) in the E-compound than in the Z ($\delta 3.29$ for $X = \text{O}$, $\delta 3.70$ for $X = \text{S}$), because of the proximity of the sulphur of the thiocarbonyl group; the deshielding effect of the thiocarbonyl group also accounts for the high chemical shift value ($\delta 8.95$ for $X = \text{O}$, $\delta 8.80$ for $X = \text{S}$) for one of the ortho-aromatic protons in the Z-product; such an effect is not seen for the E-product.

Variable temperature ^1H -NMR was used to investigate the equilibrium between the E- and Z-isomers of the α,β -unsaturated dithioesters obtained from the reaction of N-methylthiophthalimide, but no significant variation of the ratio occurred between 300 K and 328 K.

Evidence for interconversion between the E- and Z-forms of the product comes from the changes which occur on dissolving the crystalline product. The crystalline product appears

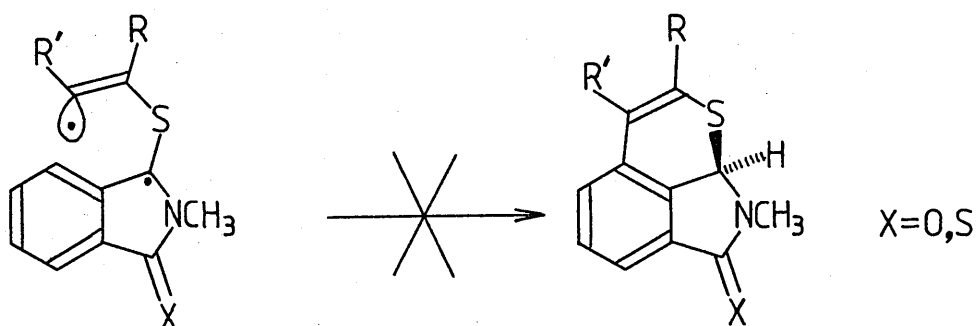
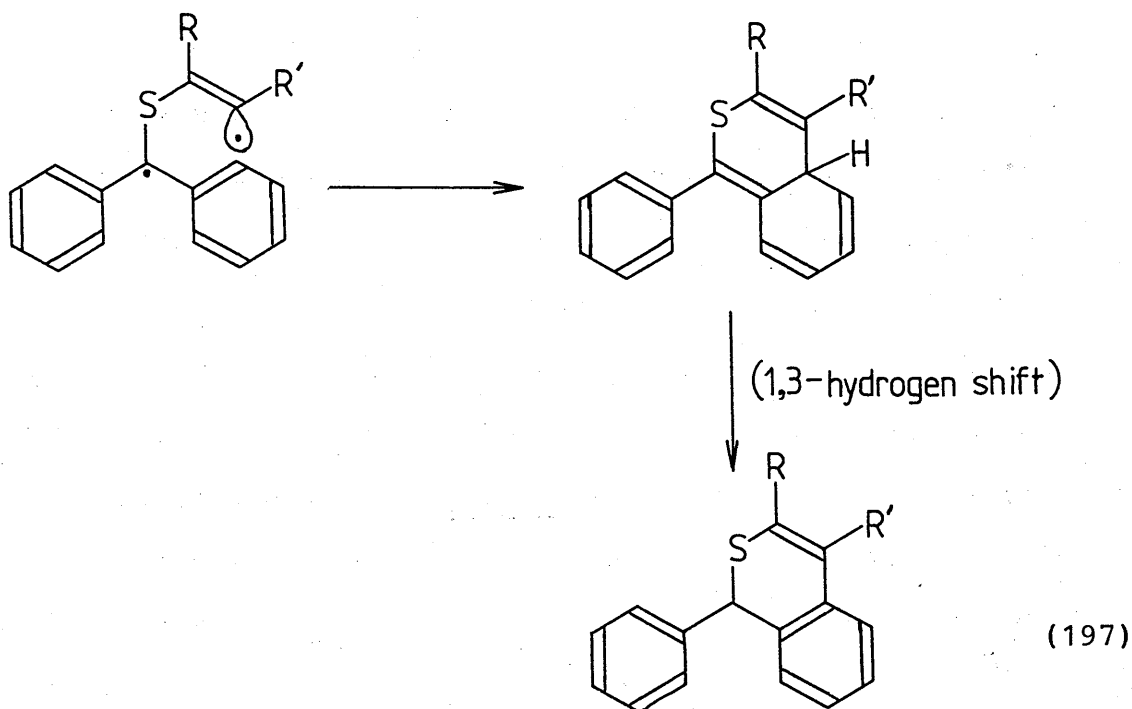
(sharp melting temperature) to contain only one product isomer - an X-ray crystallographic analysis would be required to say which - yet the solution contains the two isomeric α,β -unsaturated dithioesters (^1H - and ^{13}C -NMR). The most likely route for interconversion between the two isomers is via the spirothiete. Evidence that the spirothiete is not present at significant concentrations in solution is given by the ^1H - and ^{13}C -NMR spectra, both of which show aromatic and aliphatic absorptions for two, but not three, isomers. The ^{13}C -NMR spectrum shows two carbonyl absorptions ($\delta 167.8$ and $\delta 167.7$) and two thiocarbonyl absorptions of similar respective intensities ($\delta 228.2$ and $\delta 227.8$) for the monothioimide product.

A similar reaction was carried out for N-methylthio-phthalimide with bis(t-butylthio)ethyne. The ^1H -NMR spectrum of the product isolated (25%) from this reaction showed that it is entirely in the Z-form, which is not surprising in view of the steric bulk of the t-butylthio group (196). The yield of the pure crystalline product was rather low, mainly because sacrificial purification was required to separate it from the accompanying N-methylphthalimide.



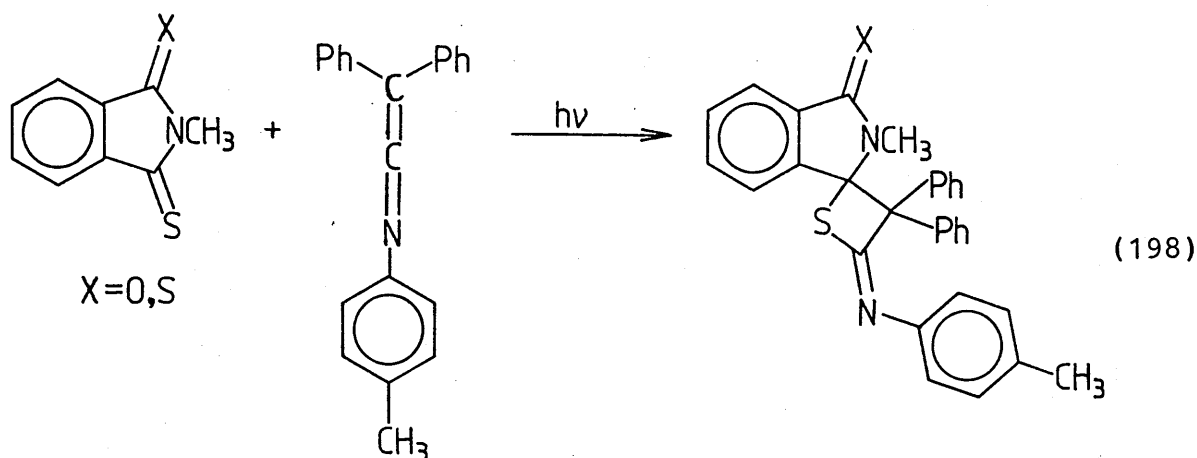
There are no reported cases of N-methylphthalimide undergoing a photocycloaddition reaction with an alkyne. The results for the N-methylthiophthalimides are parallel to those observed by Bos et al for other thiones such as thiocamphor²⁰⁷, xanthione and thiobenzophenone^{204,205}. However, as with other alkynes, no benzothiapyran products are formed in the reactions with the N-methylthiophthalimides. It is possible that this is due to a rigidity effect. In thiobenzophenone or xanthione the alkenyl radical is positioned in a six-membered ring for

ring-closure by reaction at the ortho-position of an aromatic ring, whereas for the N-methylthiophthalimide case the thio-carbonyl moiety is pulled away from the ring-closure position by the constraints of the five-membered ring. The lack of free rotation about the carbon-sulphur bond in a benzothiapyran from N-methylthiophthalimide would cause the alkene bond to be pulled out of conjugation with the aromatic ring, and give a strained thiapyran ring. Either of these factors may account for the lack of benzothiapyran products from the N-methylthiophthalimides (197).



Thioketones had been reported to react efficiently with a variety of cumulenes^{173,197,201}; it was of interest to discover whether the N-methylthiophthalimides performed equally well. This work was also carried out in collaboration with the Bos group.

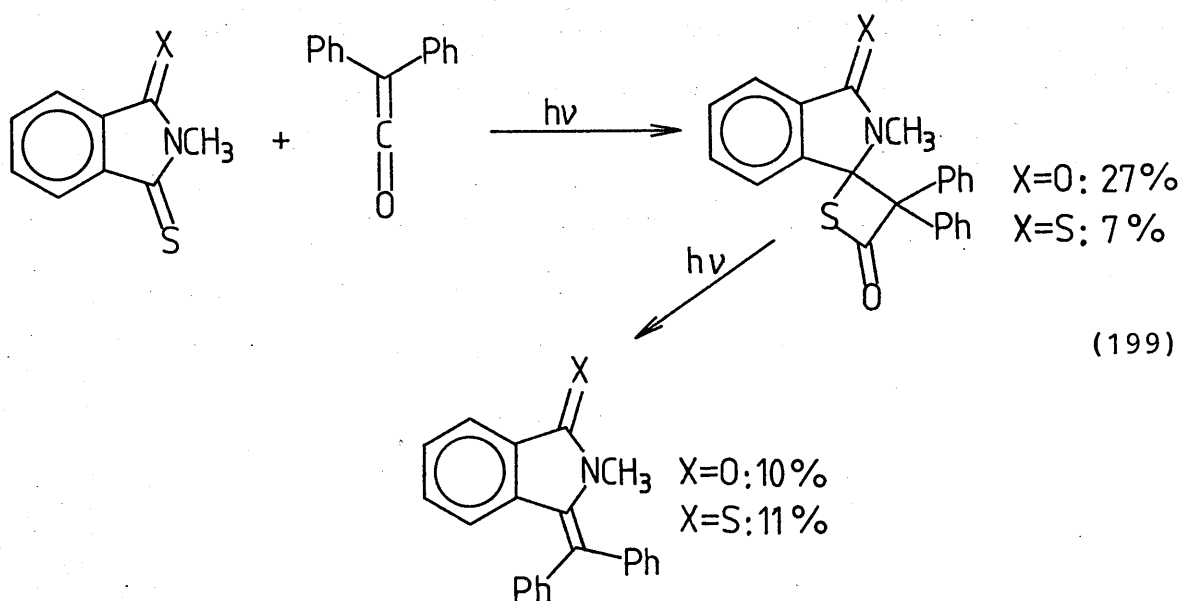
We found that N-(p-tolyl)diphenylketenimine added regio-specifically to both N-methylthiophthalimides to yield 2-imino-thietane products (198). In both cases the elemental micro-analysis results were consistent with 1:1 adducts; the mass spectra showed parent ions for 1:1 adducts at 461 ((M+H)⁺) and 476 for the monothio- and dithio-products respectively. The infrared spectra of the products showed strong C=N absorptions at 1665 cm⁻¹ and 1670 cm⁻¹ for the monothio- and dithio-products respectively, which would be appropriate for the presence of an iminothietane; the infrared spectrum of the monothio-product also showed a carbonyl absorption at 1715 cm⁻¹, which would be appropriate for a five-membered lactam. The ¹³C-NMR spectrum of the monothio-product showed absorptions for the carbonyl and C=N groups at 168.0 ppm and 160.2 ppm respectively, whereas that for the dithio-product showed a C=N group at 159.6 ppm and a thiocarbonyl group at 193.5 ppm. Both products showed many aromatic absorptions in their ¹³C-NMR spectra, together with two quaternary aliphatic carbon absorptions (81.3 and 78.1 for the monothio-product and 83.4 and 82.0 for the dithio-product), and with one NCH₃ absorption and one tolyl CH₃ absorption. Both products showed eighteen aromatic protons and two methyl singlets in their ¹H-NMR spectra, which was consistent with the proposed iminothietane structures.



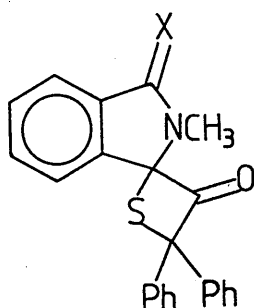
The orientation of cycloaddition was deduced from the mass spectra, which showed peaks at $m/z = 311$ and $m/z = 327$ for the monothio- and dithio-compounds respectively, corresponding to loss of a $\text{CH}_3\text{-C}_6\text{H}_4\text{-NCS}$ group; such a fragmentation is not possible for the alternative regioisomers.

The reaction of xanthione or thioxanthione with ketenimines has been shown to occur following excitation to the $S_1(n, \pi^*)$ state of the thiones²⁰¹, and it leads to iminothietane products.

We found that a similar reaction occurred for the N-methylthiophthalimides with diphenylketene (199); however, in each case two products were formed, the thietane and a product arising from loss of COS.



The structure of the thietanone products was confirmed by the spectral and analytical data. Both the monothio- and dithio-products showed elemental microanalysis results which were consistent with 1:1 thiophthalimide:diphenylketene adducts. The infrared spectra of the products showed thietanone carbonyl absorptions (1755 cm^{-1} for the monothio- and 1750 cm^{-1} for the dithio-product), and that of the monothio-product also showed a lactam carbonyl absorption at 1702 cm^{-1} . The ^{13}C -NMR spectrum also showed these carbonyl groups (181.5 ppm and 168.0 ppm for the monothio-product and 191.0 ppm for the dithio-product) together with a thiocarbonyl group for the dithio-product at 194 ppm . Both spectra also showed a number of aromatic carbon absorptions, and quaternary aliphatic carbon absorptions (75.4 ppm for the monothio-product, and 80.3 ppm and 56.6 ppm for the dithio-product) and NCH_3 absorptions (27.4 ppm and 33.0 ppm for the monothio- and dithio-products respectively). ^1H -NMR spectra of both products showed fourteen aromatic protons and a NCH_3 singlet. The mass spectra of the two products did not show parent ions: in each case the highest mass ion was attributable to $\text{M}^+ - \text{COS}$. This fragmentation showed the orientation of the product to be as shown in equation (199), and not as below (200).



$\text{X}=\text{O},\text{S}$

(200)

The structure of the monothio-diphenylmethylen product was confirmed by comparison of the ^1H -NMR and infrared spectra and the melting temperature with those of the product obtained

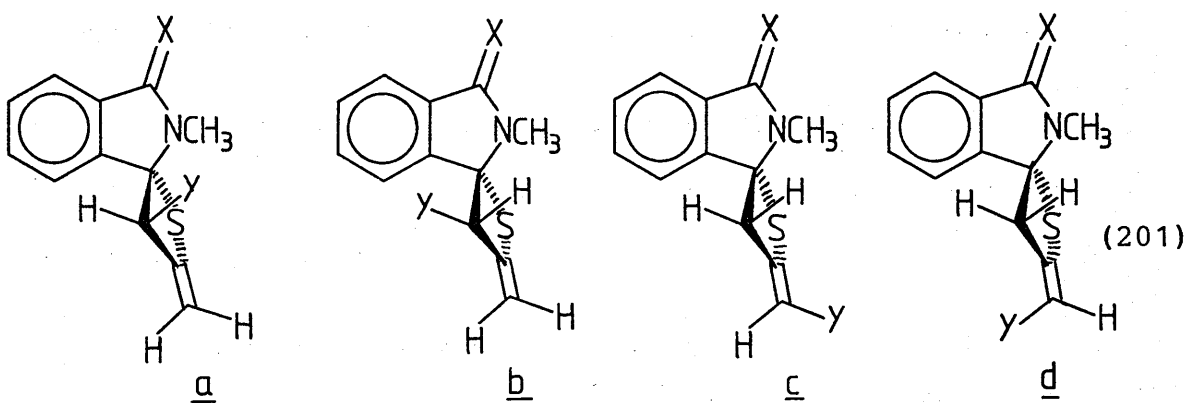
by irradiation of N-methylthiophthalimide with 1,1-diphenyl-ethene (see earlier). The structure of the dithio-diphenyl-methylene product was deduced from the analytical and spectral data. The elemental microanalysis values were consistent with those required for $C_{22}H_{17}NS$, and the mass spectrum also gave as the highest mass ion a peak at 327.108 corresponding to $C_{22}H_{17}NS$ as the molecular formula. The infrared spectrum showed no carbonyl absorption; the ^{13}C -NMR spectrum showed a thiocarbonyl absorption (191.1 ppm), a range of unsaturated and aromatic absorptions and a NCH_3 absorption (36.1 ppm), but no quaternary saturated aliphatic absorptions nor carbonyl absorption. The 1H -NMR spectrum was also consistent with the proposed structure, showing fourteen aromatic protons and a NCH_3 singlet.

We demonstrated that the second product can be produced photochemically from the thietanone by irradiating the latter using a medium-pressure mercury arc with a Pyrex filter (for the photocycloaddition reaction a high-pressure mercury arc with a $CuCl_2/CaCl_2/HCl$ filter, cut-off at about 360 nm, was employed). For both the monothio- and dithio-compounds irradiation led to a quantitative conversion of the thietanone to the second product.

Attempts to elicit the COS elimination reaction by heating the thietanone, in ethanol solution, gave rise to the N-methylthiophthalimides (i.e. cycloreversion products) in addition to the diphenylmethylene (i.e. elimination) products. The UV/VIS absorption spectra of the thietanone products show that these could have been absorbing light under the original (cycloaddition) reaction conditions (the dithio-product more strongly than the monothio-product), and overall it is likely that the

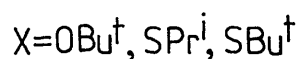
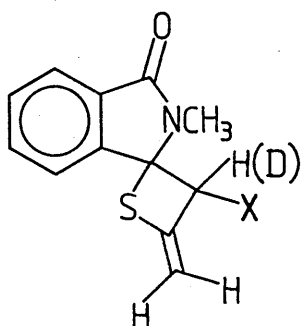
formation of the elimination products in the original reaction is a photochemical process.

Other cumulenes which had led successfully to photocycloaddition products with thioketones are allenes^{197,198}. However, a consideration of the possible products which might be obtained by reaction of allenes with the N-methylthiophthalimides shows that the situation is more complex than for the diaryl thioketones or for the ketene or ketenimine reactions with the N-methylthiophthalimides. Not only are there two possible modes of addition for an unsymmetrical allene ($\text{CH}_2=\text{C}=\text{CHY}$), but also two possible stereoisomers for each mode of addition (201).



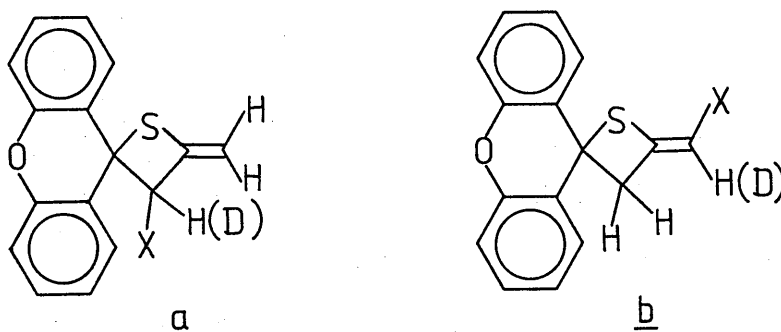
Those reactions which we tried were: N-methylthiophthalimide with t-butoxyallene, with α -D-t-butoxyallene, with isopropylthioallene, with α -D-t-butylthioallene and with m-tolylallene; N-methyldithiophthalimide with t-butoxyallene, with α -D-t-butoxyallene, with α -D-t-butylthioallene and with m-tolylallene. They all led to complex mixtures of products which could not be easily separated. Neither flash chromatography nor H.P.L.C. were successful in separating these mixtures to give single components, although unreacted allene had been removed prior to separation.

Those allene product mixtures for which some worthwhile separation was achieved were from the reactions of N-methylthiophthalimide with t-butoxyallene, α -D-t-butoxyallene, isopropylthioallene and α -D-t-butylthioallene. However, no completely pure products were obtained. All of the products which were partially purified had the orientation below (202), but it is not possible to distinguish between stereoisomers on the basis of the spectra.



(202)

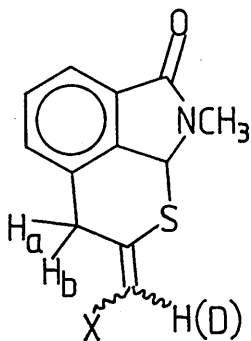
The structures were assigned following comparison of the spectral evidence with that of the products of photocycloaddition reactions of allenes with thiones^{197,198}. In the product from t-butoxyallene the chemical shifts of the three protons derived from the allene moiety are δ 5.50, δ 5.40 and δ 5.20; these are close to the values observed for the xanthione adduct of the regiochemistry shown (203a), which are δ 5.35, δ 5.10 and δ 4.98. The xanthione adduct with the alternative regiochemistry (203b) shows one proton with a chemical shift of δ 6.94, and two protons at δ 4.01. The N-methylthiophthalimide/t-butoxyallene adduct shows absorptions at 103.6, 145.3 and 81.3 ppm in the ^{13}C -NMR spectrum; the xanthione adduct with the regiochemistry shown (203a) shows absorptions at 103.6, 146.8 and 88.4 ppm for the three carbon atoms from the allene moiety.



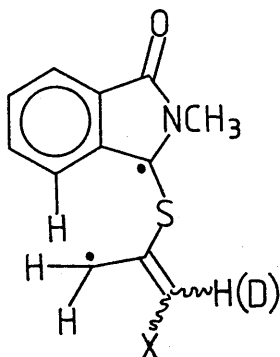
(203)

The adduct from N-methylthiophthalimide and α -D-t-butoxyallene is less pure, but shows absorptions at $\delta 5.44$, $\delta 5.40$, $\delta 5.10$ and $\delta 5.04$ in the ^1H -NMR spectrum and at $\delta 143.2$, $\delta 101.7$, $\delta 101.5$ and $\delta 79.1$ in the ^{13}C -NMR spectrum. The ^{13}C - and ^1H -NMR spectral results also suggest that these products are not thiapyrans, which would require ^1H -NMR absorptions at $\delta 6.3$ and $\delta 5.7$, and ^{13}C -NMR absorptions near to $\delta 113$ and $\delta 34$. The chemical shifts observed in the ^1H -NMR spectrum for the protons derived from the allene moiety in the adduct of N-methylthiophthalimide with isopropylthioallene are $\delta 5.61$, $\delta 5.57$, $\delta 5.49$, $\delta 5.20$, $\delta 5.18$ and $\delta 5.13$ and in the ^{13}C -NMR absorptions are seen at $\delta 145.5$, $\delta 105.3$ and $\delta 104.7$; no direct comparison is available for this compound, but these values are consistent with the xanthione/methylthioallene adduct of regiochemistry (203a), which shows ^1H -NMR absorptions at $\delta 5.43$, $\delta 5.09$ and $\delta 4.98$ ($\delta 5.97$ and $\delta 4.08$ for regiochemistry (203b)) and ^{13}C -NMR absorptions at $\delta 105.0$ and $\delta 141.1$. Similarly the product from N-methylthiophthalimide with α -D-t-butylthioallene shows ^1H -NMR absorptions at $\delta 5.50$, $\delta 5.05$ and $\delta 4.80$ and ^{13}C -NMR absorptions at $\delta 143.2$, $\delta 103.0$ and $\delta 102.5$, which compare well with the absorptions for the corresponding xanthione adduct of regiochemistry (203a) which shows ^1H -NMR absorptions at $\delta 5.49$ and $\delta 5.06$ ($\delta 6.09$ and $\delta 4.07$ for regiochemistry (203b)), and ^{13}C -NMR absorptions at $\delta 144.8$ and $\delta 104.2$.

It is possible that products formed from the alternative orientation of photocycloaddition of the allene might be present in the mixtures, as this is the case for thioketones; it is also possible that they may decompose more readily during work-up, as they would be susceptible to acid attack. The N-methylthiophthalimide reactions do not yield any pure (4+2)-thiapyran products (204), but their presence in the crude reaction mixtures cannot be ruled out. Such products would be expected to show absorptions close to $\delta 6.2$, $\delta 5.7$ and $\delta 3.4$ in the ^1H -NMR spectrum, and close to $\delta 77$ and $\delta 35$ in the ^{13}C -NMR spectrum, by comparison with thiapyran products obtained as minor products in the photocycloaddition reaction of xanthione with allenes¹⁹⁷; the ^1H -NMR spectra of the crude reaction mixtures of N-methylthiophthalimide with t-butoxyallene, α -D-t-butoxyallene and α -D-t-butylthioallene all show absorptions close to $\delta 6.2$ and $\delta 5.7$. Absorptions close to $\delta 3.2$ are also seen in all of these reaction mixtures, although these are singlets rather than the multiplets which might be expected for H_a and H_b , and are probably attributable to NCH_3 protons, in which case it would appear that thiapyran products are not present. The crude reaction mixture from the reaction of N-methylthiophthalimide with isopropylthioallene is shown not to contain any thiapyran products, as there are no signals near to $\delta 6.2$ in the ^1H -NMR spectrum of the crude reaction mixture. The formation of thiapyran adducts would seem less likely than the formation of thietanes, as the closure of the possible intermediate biradical (205) to form a thiapyran would be more sterically hindered than closure to form a thietane, on account of the proximity of the hydrogen atoms of the methylene radical group to the hydrogen atom at the ring-closure position of the aromatic group.



(204)

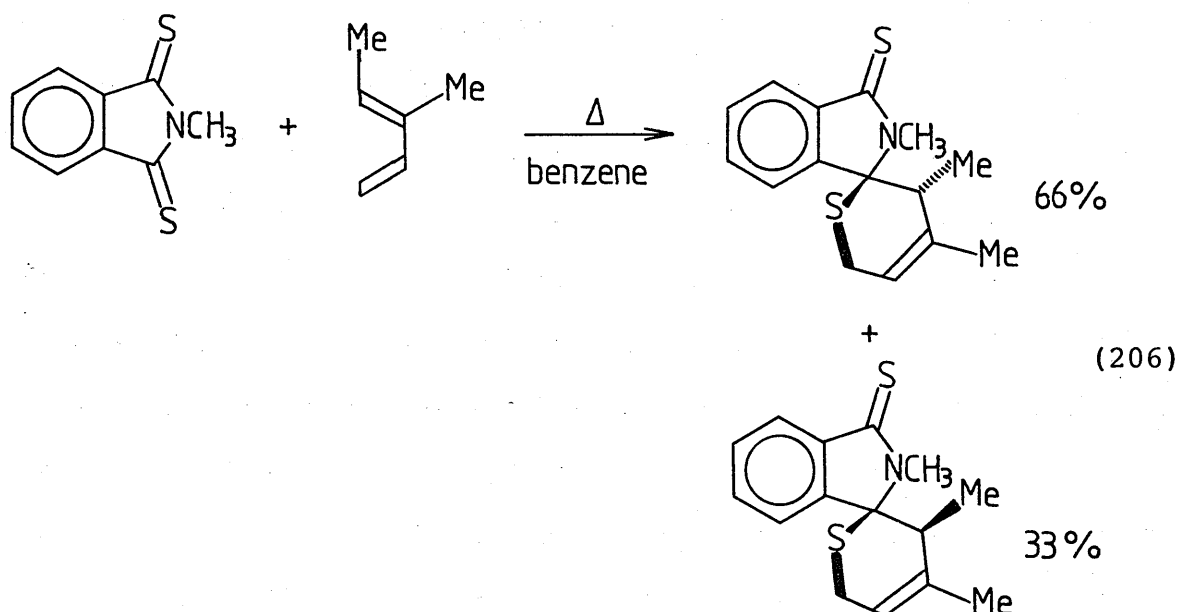


(205)

Most of the allene reactions were carried out using a high-pressure mercury arc with a $\text{CuCl}_2/\text{CaCl}_2/\text{HCl}$ filter solution (cut-off at about 360 nm); irradiations with *m*-tolylallene using a medium-pressure mercury arc with a Pyrex filter were performed, but the ^1H -NMR spectra of the product mixtures obtained from these reactions were no less complex than those from the high-pressure mercury arc reactions.

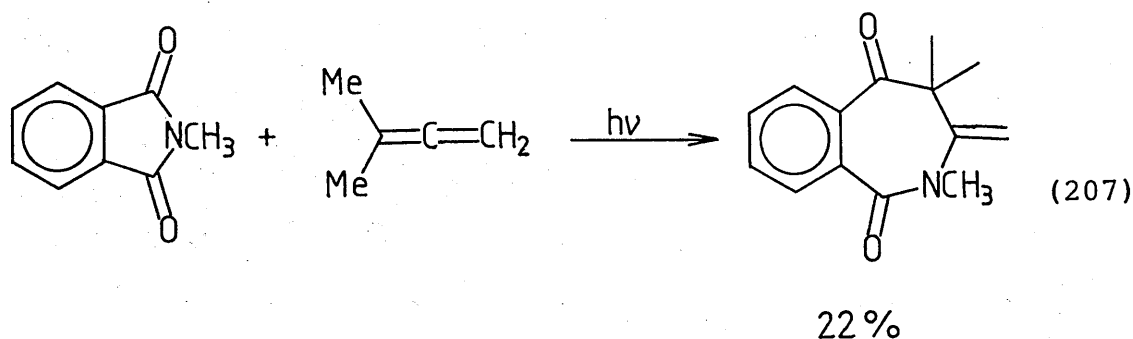
In control experiments we found that whereas *N*-methylthiophthalimide is unreactive towards allenes in the dark at room temperature, *N*-methyldithiophthalimide reacts thermally with allenes to give complex product mixtures, and so the photochemical cycloaddition reactions were carried out with the reaction vessel immersed in a cardice/acetone bath. This was the only system of all those that we have studied in which a thermal reaction occurred at a rate which was competitive with the photochemical reaction rate under the conditions used; for all other photocycloaddition reactions any thermal reactions

were found to be very much less efficient or completely non-existent. Thiones are known to undergo thermal cycloaddition reactions to allenes^{198,227} and a rather slow (0.5 to 5 days at room temperature) thermal cycloaddition reaction is reported for N-methyldithiophthalimide acting as a heterodienophile in a Diels-Alder reaction (206)¹⁹¹.



(This is in contrast with the photochemical cycloaddition of 2,5-dimethylhexa-2,4-diene to N-methyldithiophthalimide¹¹⁰, in which the primary product is a thietane.)

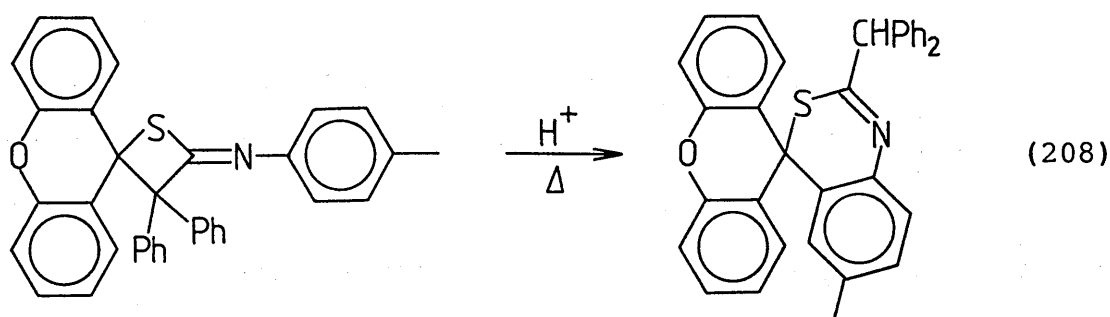
The photoreaction of allenes with thioketones has been well studied by Gotthardt^{179,194}, and also by Bos and Kamphuis¹⁹⁶⁻⁸, whose work shows that the reaction proceeds from the $T_1(n, \pi^*)$ state of the thione, and that a 1,4-biradical intermediate is involved. The reactions of N-methylphthalimide with cumulenes have not been widely investigated: there is only one reported reaction of N-methylphthalimide undergoing photocycloaddition with an allene⁴⁶, to give a benzazepinedione, which is comparable to the products from alkene photocycloaddition reactions (207).



The great majority of our photoproducts from the N-methylthiophthalimides with multiply-bonded addends contain a four-membered sulphur-containing ring. Since some thietanes are known to be sensitive to heat and/or acids²²⁸, we therefore investigated the stabilities of some of our photoproducts under these conditions. It was found that the major thietane product from the reaction of N-methylthiophthalimide with trans-stilbene was resistant to heat (two hours at 80 °C) in the presence of benzenesulphonic acid. The effect of heat and acid on the thiete product from the reaction of N-methylthiophthalimide with diphenylethyne was apparently very little after two hours (as seen on T.L.C.); refluxing in absolute ethanol with benzenesulphonic acid for twenty-four hours led to decomposition to several products (as seen by ¹H-NMR), whereas refluxing in absolute ethanol for twenty-four hours with no acid present led to only a small degree of decomposition. It was found that if a sample of this thiete was melted and then cooled slowly, some decomposition occurred. No product was isolated.

It was thought that the iminothietane products formed in the reactions of the N-methylthiophthalimides with the ketenimine might rearrange on heating in the presence of a little benzenesulphonic acid to form a benzothiazine; such a reaction has been observed for the iminothietane products from

xanthione and thioxanthione (208)²⁰¹. In the case of the N-methyldithiophthalimide product, heating in ethanol solution at 90 °C in the presence of benzenesulphonic acid led to a mixture of products including cycloreversion products (T.L.C. and ¹H-NMR). Although there were some absorptions in the ¹H-NMR spectrum at δ 5.40, δ 5.10 and δ 5.00 which could have indicated the formation of a benzothiazine (broad s expected at δ 5.10)²²⁹, it is obvious that this is not a clean reaction. Similar experiments were carried out for the N-methylthiophthalimide product using both ethanol and chloroform solutions, but again the main reaction was cycloreversion, and benzothiazine formation is a minor reaction if it is happening at all.



The general conclusions which may be drawn from the results of our studies relating to photocycloaddition reactions of the N-methylthiophthalimides are:

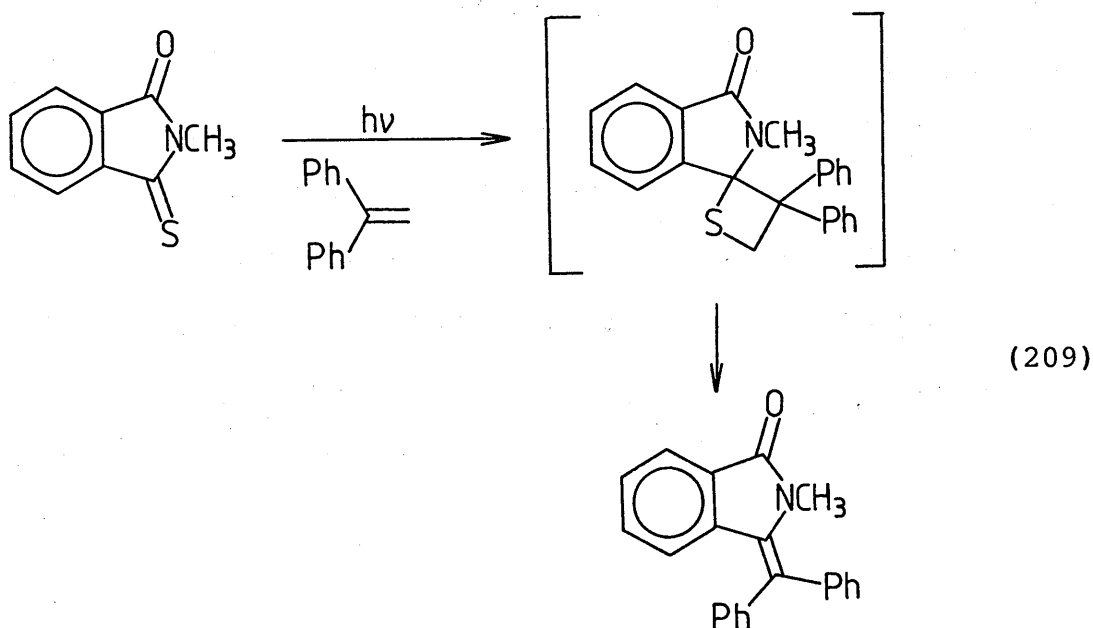
- (i) they occur at the thiocarbonyl rather than the carbonyl bond (possible reasons for this are discussed in the next chapter);
- (ii) they resemble those of other thiocarbonyl compounds, in giving mainly four-membered ring products (thietanes, thietes), or products derived therefrom, or 1,4-dithianes; they are unlike most photocycloaddition reactions of the corresponding phthalimides, which give mainly benzazepinedione products;

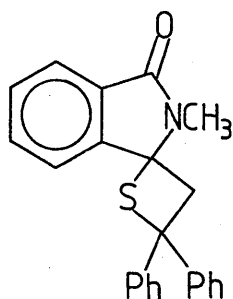
- (iii) they are regioselective, as demonstrated by results from the 1,1-diphenylethene reaction, the ketene reactions and the ketenimine reactions;
- (iv) they may be non-stereospecific, as suggested by results from the reactions with cis- and trans-stilbene.

The $T(n, \pi^*)$ state might be expected to be the reactive state by analogy with the reactions of other thiocarbonyl compounds, as described throughout, and also by comparison with the N-methylphthalimide case in which the relatively unusual oxetane products arise from a triplet state reaction, whereas the major benzazepinedione products arise from an $S_1(n, \pi^*)$ reaction. For the N-methylthiophthalimides intersystem crossing would be expected to be more efficient than for N-methylphthalimide because the presence of sulphur leads to greater relaxation of the selection rules. It seems less likely that S_2 is the reactive state because of the regioselectivity, and, for the stilbenes, non-stereospecificity, of the reactions: for other thiocarbonyl compounds such as adamantanethione⁷⁸, di-t-butylthione¹⁷⁶, thiobenzophenone¹⁶⁷ and xanthione¹⁷⁵ the S_2 reaction has been shown to be stereoselective but non-regioselective, whereas the $T_1(n, \pi^*)$ reaction has been shown to be regioselective but non-stereoselective. Support for reaction from T_1 (or S_1) but not S_2 comes from our observations for the N-methylthiophthalimides that reaction will occur following excitation to S_1 only (as with N-methyl-dithiophthalimide reacting with bis(methylthio)ethyne, or N-methylphthalimide reacting with bis(t-butylthio)ethyne), and that such a reaction is efficient in terms of percentage conversion, time taken and chemical yield of products. This proposal that reaction occurs from T_1 is further supported by

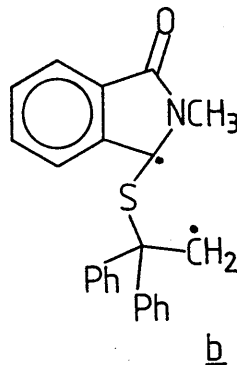
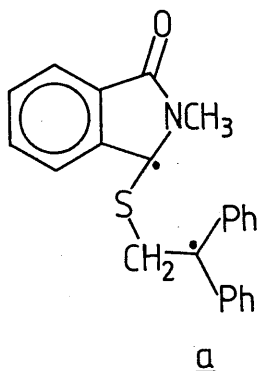
the photophysical results (Chapter Four) which show that excitation of N-methylthiophthalimide to the S_2 state leads to the same emission as follows excitation to the S_1 state, indicating that internal conversion from S_2 to S_1 is very rapid. Quenching experiments, using each of the N-methylthiophthalimides with bis(methylthio)ethyne or allenes as added quenchers, showed quenching of a triplet transient, which also supports the suggestion that photocycloaddition reactions occur from the $T(n,\pi^*)$ state. However sensitisation and quenching experiments would be required to test this idea further.

The likelihood of a 1,4-biradical intermediate is suggested by the regioselectivity of the reactions. For example, for 1,1-diphenylethene, the formation of (209) as major product, rather than (210), can be accounted for in terms of the more highly stabilised biradical (211a) as intermediate, rather than (211b).



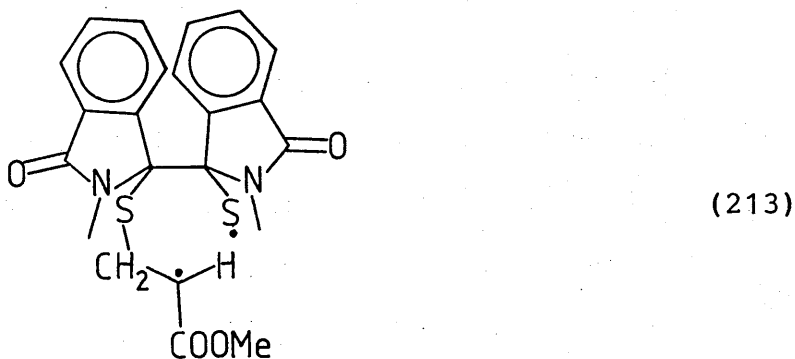
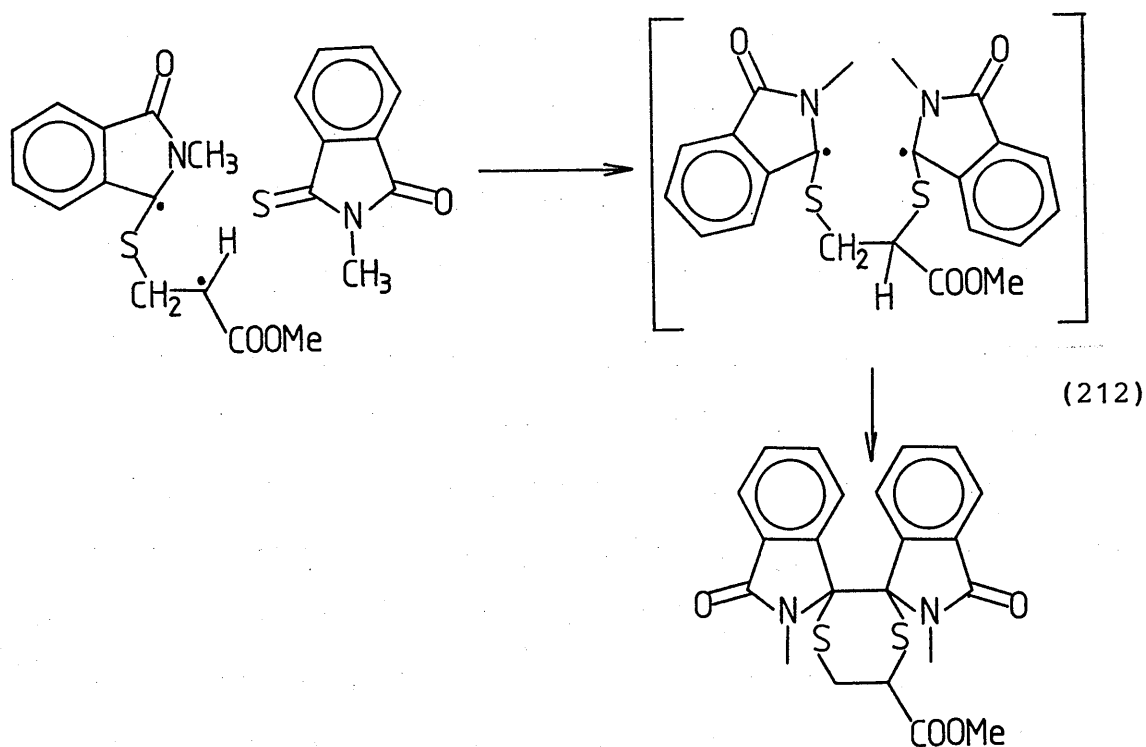


(210)



(211)

Another observation which supports the proposal of an intermediate 1,4-biradical is the formation of 1,4-dithianes, which are readily rationalised on the basis of trapping of a 1,4-biradical by a molecule of ground state thioimide (212). The biradical intermediate is drawn as shown in (212) rather than as (213), as the former would be expected to be stabilised by a captodative effect (see later).



One general feature of our results is that the reactions of N-methyldithiophthalimide often occur less readily or with lower efficiency than those of N-methylthiophthalimide. This may be because the reactive state has a lower energy: the energy of the emitting state in the dithio-compound is about 184 kJ mol^{-1} , compared to about 217 kJ mol^{-1} for the monothio-compound. However, the triplet energy of thiobenzophenone⁷⁹, which reacts efficiently from the triplet state, is 159 kJ mol^{-1} , and so this may be only part of the explanation.

A further possibility is that the stabilisation of a biradical intermediate would be considerably more effective for the monothio-compound because of a captodative effect arising from electron-donating (N,S) and electron-withdrawing ($C=C=O$) substituents (214, $X = O$). The $C=C=S$ group in the corresponding biradical from the dithio-compound (214, $X = S$) is less effective as an electron-withdrawer.



$X=O,S$

(214)

CHAPTER THREE

PHOTOCHEMISTRY OF THIOPHTHALIMIDES:

OTHER REACTIONS

RESULTS AND DISCUSSION

Photooxidation

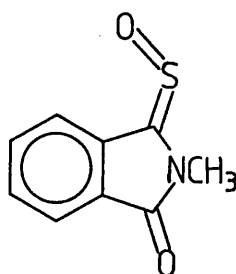
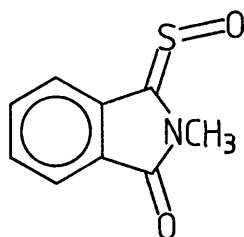
Our interest in the photooxidation reactions of N-methylthiophthalimides arose from the discovery of small quantities of oxidised products in the mixtures obtained on irradiation of the thiophthalimides. All of the photocycloaddition reactions of N-methylthiophthalimide yielded a small amount of N-methylphthalimide among the products, and one of the irradiations of N-(morpholinomethyl)thiophthalimide gave N-(morpholinomethyl)phthalimide as a minor product. We also wished to compare the behaviour of the N-methylthiophthalimides with the known photooxidation reactions of other thiocarbonyl compounds.

Irradiation of N-methylthiophthalimide in the presence of oxygen led to the formation of N-methylphthalimide, in 66% isolated yield, as the only organic product. The reaction was repeated in order to determine the yields of sulphur and sulphur dioxide: these were 48% and 3% respectively. Irradiation of N-methyldithiophthalimide under similar conditions led to the formation of N-methylthiophthalimide as the initial product; this was then oxidised in situ to N-methylphthalimide. Elemental sulphur was also seen to deposit on the walls of the reaction vessel. The isolated yield of pure N-methylphthalimide from the photooxidation of N-methyldithiophthalimide was 45%. The reason for the fairly low isolated yield of the imide both in this reaction and in the N-methylthiophthalimide photooxidation is that not all of the elemental sulphur is removed by filtration through a sinter, and so the recrystallisation does not easily yield pure crystals.

The yield (48%) of sulphur obtained by filtration following the photooxidation of N-methylthiophthalimide is probably considerably lower than the overall yield because of the scale of the irradiation (maximum yield of sulphur is 40 mg). Elemental sulphur is deposited on the walls of the vessel during the reaction, and some of this is inevitably lost in the scraping and filtration process.

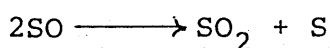
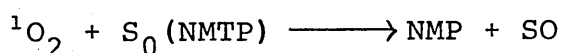
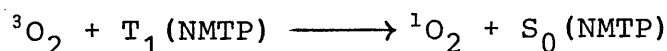
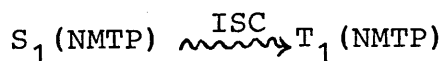
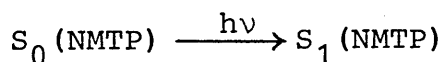
The very low yield (3%) of barium sulphate isolated in the sulphur dioxide determination^{230,231} is likely to be because most of the sulphur dioxide passed through the sodium hydroxide solution without reacting. However, the results are still important in a qualitative sense, and the lack of quantitative agreement is most probably due to experimental factors in this single determination.

It is interesting that the sole oxidation products are the N-methyl(thio)phthalimide, sulphur and sulphur dioxide, and that no evidence (T.L.C., IR or ¹H-NMR) exists for any sulphine product (215), as is observed by some workers for thioaryl amides¹³⁶, and for alkyl aryl thioketones²³². Such products would be expected to show NMe absorptions in the ¹H-NMR spectra different to those seen for N-methyl(thio)phthalimide. They would also be likely to show separate spots on T.L.C., and to be among the non-volatile products isolated at the end of the reaction.

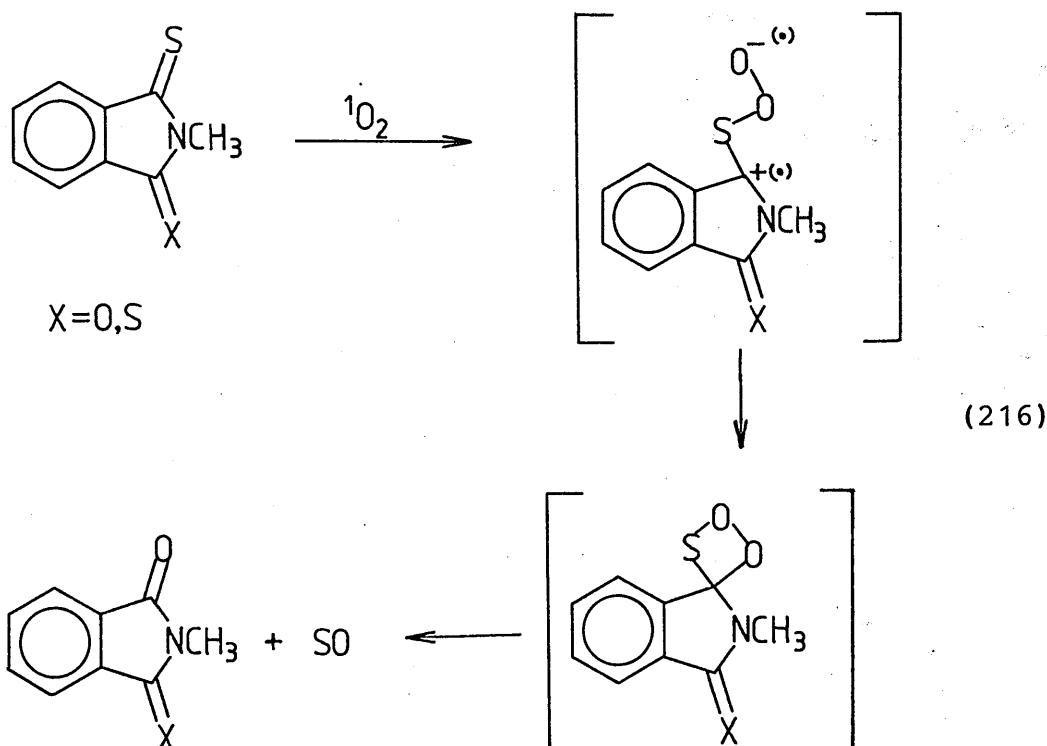


(215)

By comparison with the photooxidation reactions of other thiocarbonyl compounds²³², it is possible that the mechanism for the N-methylthiophthalimides (NMTP) is via singlet oxygen:



The formation of the analogous carbonyl compound as the only product parallels the reaction of diaryl thioketones. As with the thiocarbonyl group in diaryl thioketones, the thiocarbonyl group in N-methylthiophthalimides is part of an extended conjugated system, which could stabilise a zwitterionic/biradical intermediate as shown (216). A 1,2,3-dioxathietane is a possible intermediate in these reactions.



Although the existence of a pathway involving reaction between excited thioketone and triplet oxygen cannot be completely ruled out, it would be unexpected by comparison with the results for thioketones^{124,125}. We have shown in dark control reactions that there is no reaction at room temperature between ground-state thiophthalimide and triplet oxygen.

An indication of the efficiency of the reaction of oxygen with the N-methylthiophthalimides may be obtained from the photocycloaddition reactions, in which the isolation of photo-oxidation products shows that there is some competition between reaction of the excited N-methylthiophthalimide with triplet oxygen (probably energy transfer to form singlet oxygen) and reaction with the multiply-bonded compound. White-spot grade nitrogen was used for all reactions; this contains 0.0005% oxygen, and the flow-rate of the nitrogen ($\sim 0.5 \text{ cm}^3 \text{ s}^{-1}$) for the time scale of a photocycloaddition reaction (up to fifty hours) would indicate that the quantity of oxygen becomes significant. Solubility of oxygen in the solvent ($\sim 1 \text{ g cm}^3$) would not be a limiting factor. The quantum yield of singlet oxygen production for thioketones¹²² is high (~ 0.8 at 0.01 M concentration), and so singlet oxygen production by the N-methylthiophthalimides might be expected to be efficient.

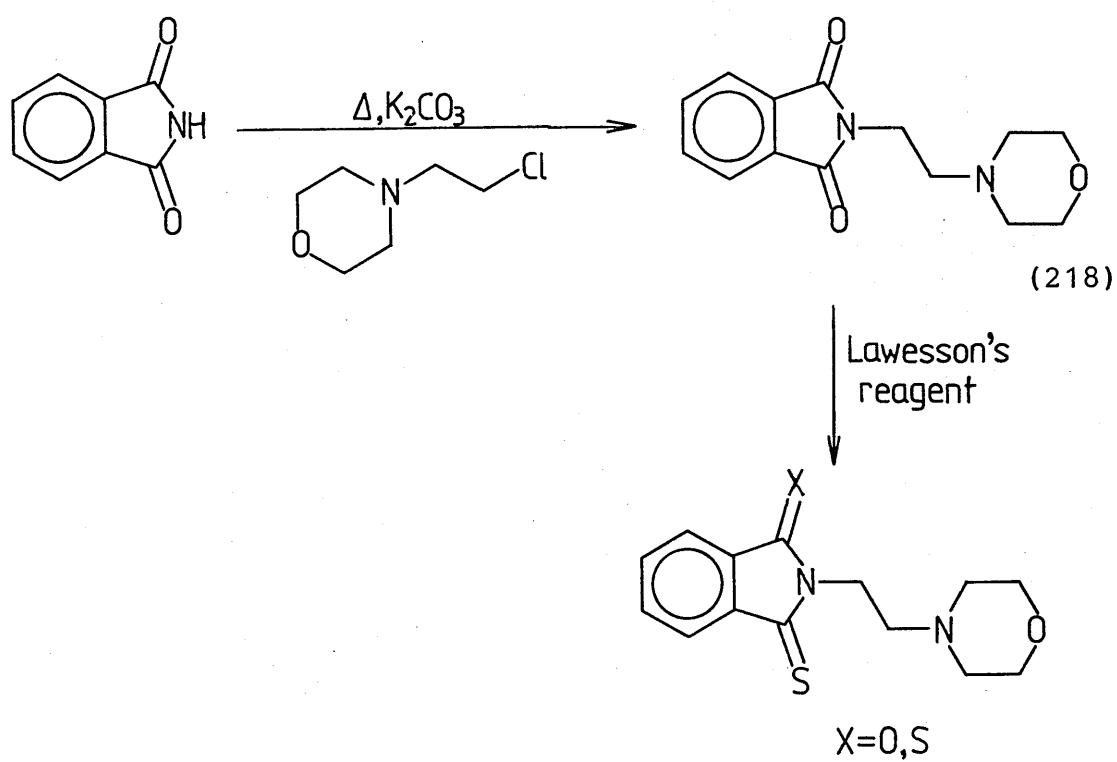
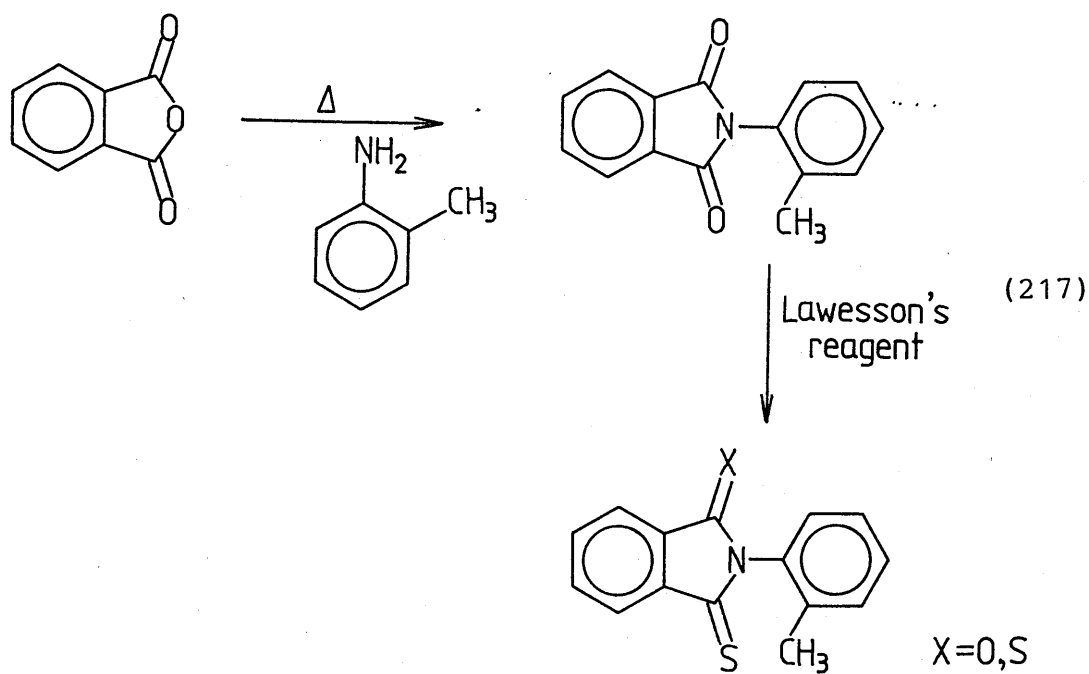
Hydrogen abstraction reactions

Both thioketones and phthalimides give rise to a variety of products following intermolecular or intramolecular hydrogen abstraction, and such reactions may be used in the preparation of heterocyclic systems. It is therefore of interest to investigate reactions of thiophthalimides in which hydrogen abstraction is potentially feasible.

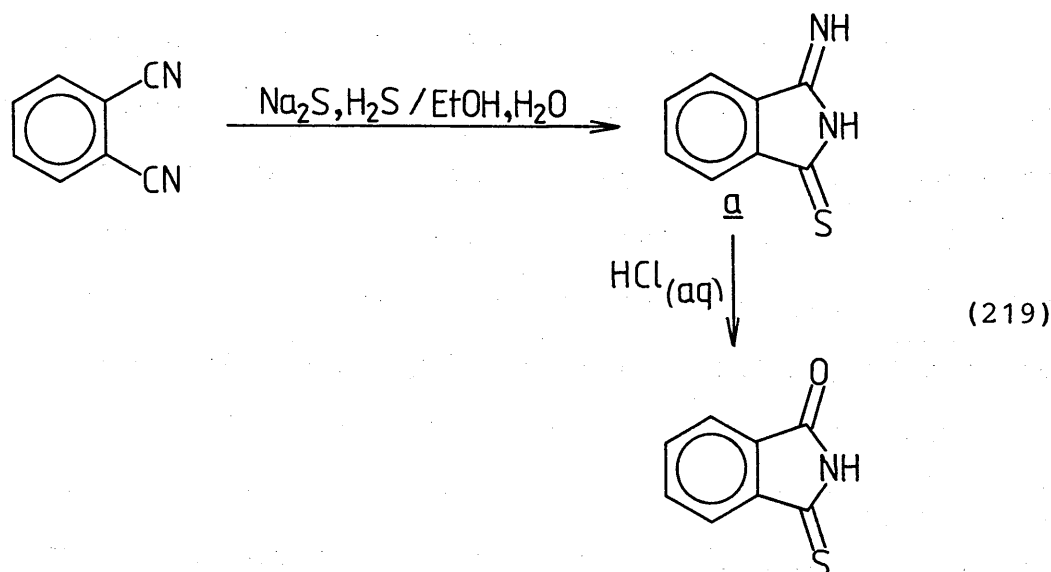
The compounds used in these investigations were N-methylthiophthalimide, N-isobutylthiophthalimide, N-o-tolylthiophthalimide, N-o-tolyldithiophthalimide, N-(2-morpholinoethyl)thiophthalimide, N-(2-morpholinoethyl)dithiophthalimide and a range of N-(dialkylaminomethyl)thiophthalimides.

Preparations

N-Methylthiophthalimide was prepared using Lawesson's reagent as described in Chapter Two. N-Isobutylthiophthalimide was prepared from thiophthalimide and 1-bromo-2-methylpropane using the N-alkylation method described in Chapter Two for the first preparation of N-methylthiophthalimide. The N-o-tolylthiophthalimides were both prepared by a thiation reaction using Lawesson's reagent on the corresponding N-substituted phthalimide. N-o-Tolylphthalimide was prepared from phthalic anhydride and o-toluidine according to a standard method (217)²²⁰, and N-(2-morpholinoethyl)phthalimide was prepared using N-(2-chloroethyl)morpholine and phthalimide (218)²²⁰.

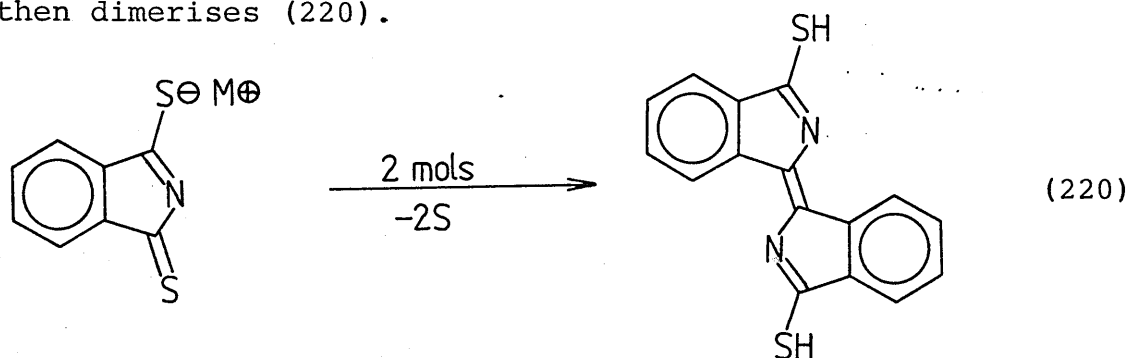


The N-(dialkylaminomethyl)thiophthalimides were prepared from unsubstituted thiophthalimide; the preparations of these compounds will be discussed in some detail. The main method of preparation used for thiophthalimide was that of Porter, Robinson and Wyler (219)²³³. One attempt to prepare thiophthalimide using Lawesson's reagent²¹⁹ led to a sample which was contaminated with phthalimide, although this method of thiation was found to be a good route to dithiophthalimide.



In contrast to the literature report, we found that no yellowish brown needles of 3-imino-2,3-dihydroisoindoline-1-thione (219a)²³⁴ were obtained following the passage of hydrogen sulphide through the suspension of 1,2-dicyanobenzene, and also that the suspension became brownish-purple in colour during the reaction. This colour may be attributed to the formation of by-products such as dithio- β -isoindigo as described by Drew and Kelly²³⁵, who suggest that 1,2-dicyanobenzene reacts with excess sodium hydrogen sulphide or

hydrogen sulphide to give dithiophthalimide as a salt which then dimerises (220).

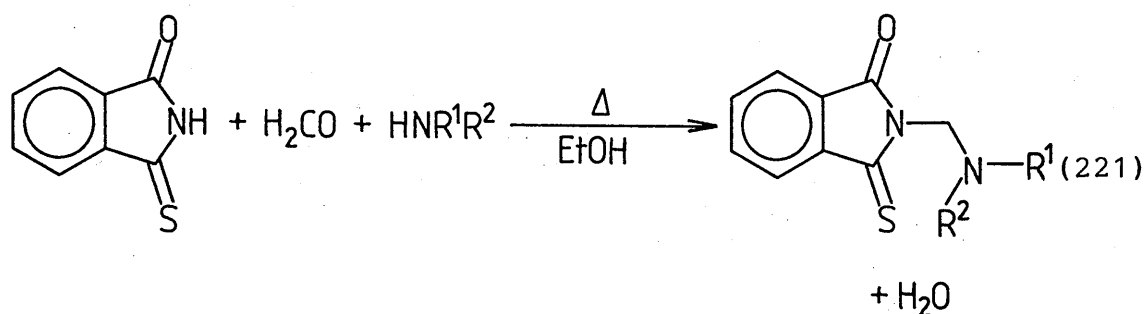


The time taken for passing hydrogen sulphide through the reaction mixture was reported as being six hours ^{233,235}. In our laboratories it was found that for maximum conversion of 1,2-dicyanobenzene to 3-imino-2,3-dihydroisoindoline-1-thione it was necessary to pass hydrogen sulphide through the suspension for eight hours and then to leave the reaction mixture standing overnight. Although this method produced a brown slurry rather than yellow needles, it ensured the complete conversion of 1,2-dicyanobenzene, which is more difficult to separate from the final thiophthalimide than are the dark coloured products. Similar results were obtained by Mahoney²³⁶, following the passage of hydrogen sulphide for four hours and leaving the mixture to stand overnight. It is possible that the variation in results from this reaction arises from it being a heterogeneous reaction; a temperature dependence has also been noted ²³⁶, which showed the optimum temperature of reaction to be 20-25 °C.

The second step, hydrolysis of the 3-imino-2,3-dihydroisoindoline-1-thione to form thiophthalimide, was straightforward.

Phthalimides readily form Mannich bases, N-(dialkylaminomethyl)phthalimides, with formaldehyde and secondary amines, but there have been no literature reports for the

preparation of Mannich bases from thioimides, and only one for a thioamide²³⁷. The general method for their preparation employed thiophthalimide, 40% formaldehyde solution and a secondary amine in ethanol solution (221). A summary of the results is given in Table 3.1.



<u>Secondary amine</u>	<u>Yield of Mannich base</u>
Dibenzylamine	29%
1,2,3,4-Tetrahydroisoquinoline	74%
Morpholine	67%
Piperidine	72%
Dimethylamine	(4%) Unsuccessful preparation
1,2,3,6-Tetrahydropyridine	Unsuccessful preparation
<u>N</u> -Methylbenzylamine	Unsuccessful preparation
<u>N</u> -Methylcyclohexylamine	(3%) Unsuccessful preparation
Dicyclohexylamine	70%

Table 3.1: Preparation of thiophthalimide Mannich bases

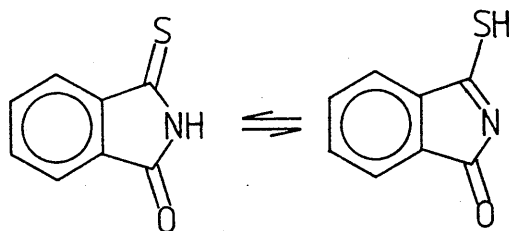
The morpholine and the 1,2,3,4-tetrahydroisoquinoline Mannich bases sometimes separated as an oil and sometimes crystallised without difficulty. In the case of dimethylamine a yellow-brown solid was found to precipitate out during the recrystallisation of the solid. The formation of this solid

was shown to be an equilibrium process, in that if it were filtered off then more precipitated out. As it was insoluble in boiling ethanol, and as a nujol mull infrared spectrum of the sample showed little more than nujol absorptions, it is possible that this solid was elemental sulphur. For 1,2,3,6-tetrahydropyridine it was clear that some reaction had taken place, as an oil separated out of the reaction mixture on cooling. Column chromatography of the oil led to two fractions, the first an orange oil containing three components as seen on T.L.C., and the second a yellow oil containing four components as seen on T.L.C.; the latter fraction was seen by ^{13}C -NMR to contain no thiocarbonyl group. This reaction was not investigated further. In the case of N-methylbenzylamine an oil separated out from the reaction mixture; this proved resistant to crystallisation. Column chromatography led to four impure fractions. Preparation of the N-methylcyclohexylamine Mannich base was tried using the hydrochloride method, in which the ethanol is removed from the reaction mixture in vacuo, and the oily residue is dissolved in dry ether which is then saturated with hydrogen chloride gas in order to produce the Mannich base hydrochloride. The resulting solid could not be recrystallised from ethanol or propan-2-ol, and so it was neutralised. An attempt to recrystallise the sample from ethanol led to the precipitation of a brown amorphous solid; this was removed by filtration and the crystals which were eventually obtained, by a further recrystallisation from ethanol of the evaporated mother liquor, were in low yield (3%) and impure (the solid had two melting ranges - 114-116 °C, and around 122 °C).

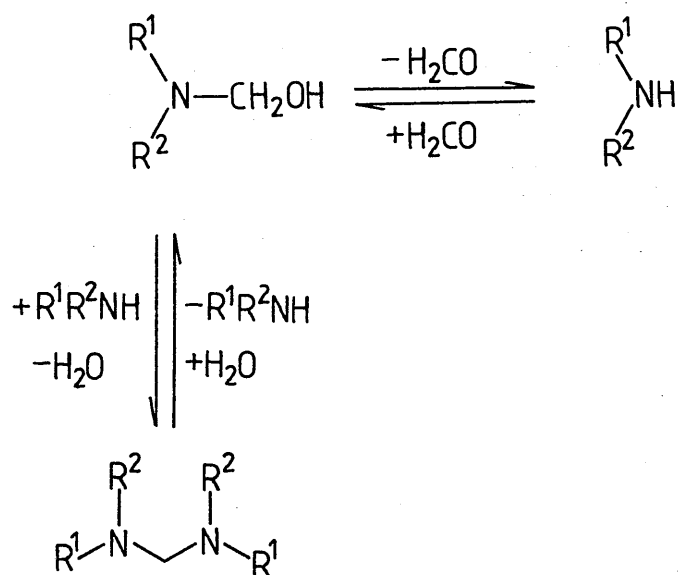
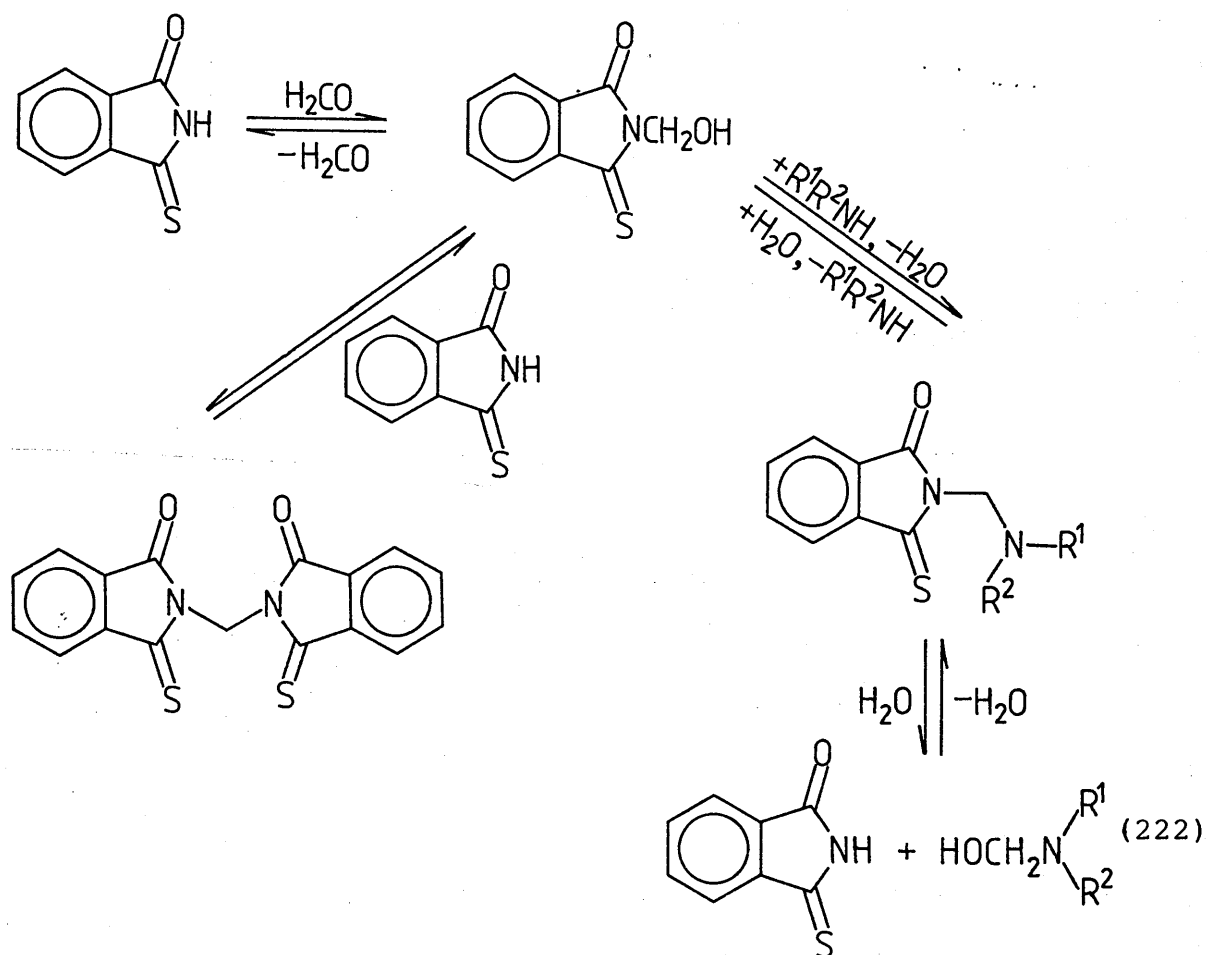
Mahoney²³⁶ also experienced difficulties in the preparation of some of the thiophthalimide Mannich bases; he found that the

dibenzylamine and 1,2,3,4-tetrahydroisoquinoline Mannich bases were easily prepared, whereas the attempted preparations of the diallylamine and pyrrolidine Mannich bases led to dark-coloured oils, and his attempted preparation of the piperidine Mannich base under acid conditions gave N-(hydroxymethyl)thiophthalimide.

The problems associated with the Mannich reaction are those of competing equilibria(222)^{238,239} In addition, thiophthalimide has the added complication that the thione-enethiol tautomerisation (223) is more favourable than the keto-enol tautomerisation for phthalimide, and although the enethiol form is estimated to be at a low concentration compared to the thione form²⁵², it is possible that reaction could occur at the sulphur atom rather than the nitrogen atom.



(223)



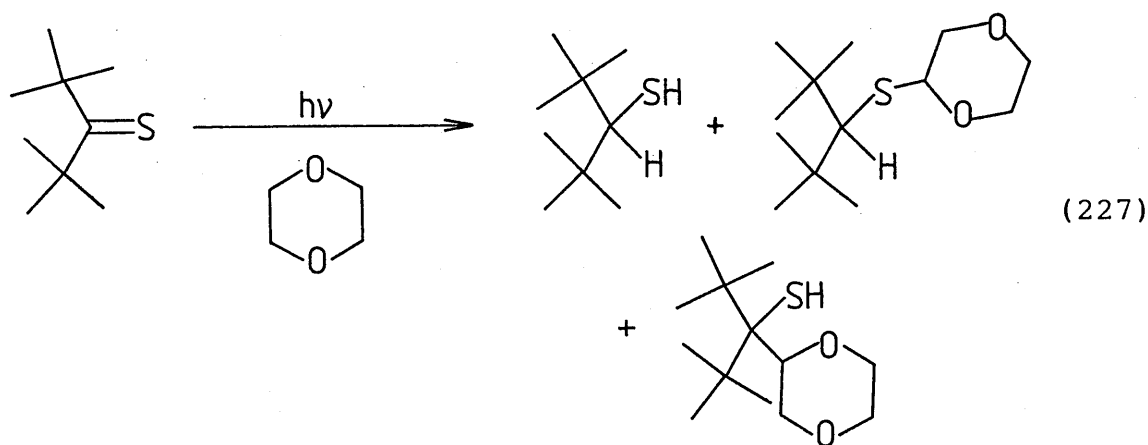
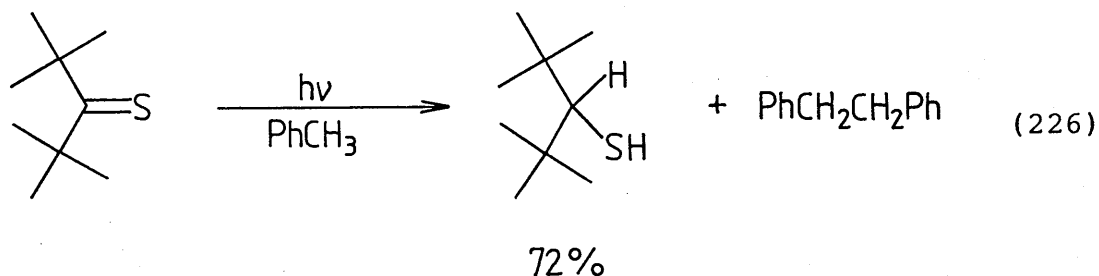
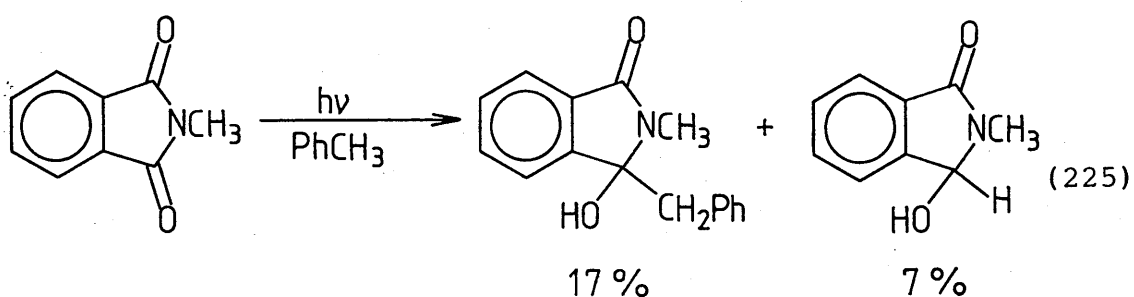
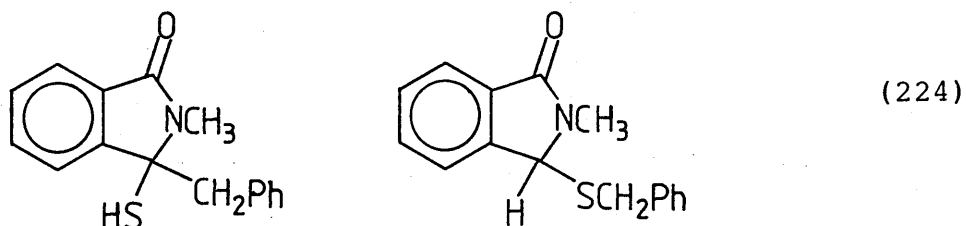
It might be interesting to try to overcome the difficulties in the preparation of thiophthalimide Mannich bases by employing the alternative route of thiation, using Lawesson's reagent, of the corresponding phthalimide Mannich bases, which are easily prepared.

Irradiations

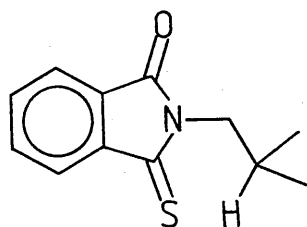
In order to determine whether intermolecular hydrogen abstraction takes place for thiophthalimides, N-methylthiophthalimide was irradiated in toluene. Toluene might be expected to be a good candidate for intermolecular hydrogen abstraction in view of the stabilisation by the aromatic group in the benzyl radical formed by removal of a hydrogen atom from the methyl group. The irradiation led to a mixture of products, but none could be isolated in a state pure enough for characterisation. Separation by column chromatography gave unreacted starting material as the first fraction. As only 20% of the starting material was recovered unchanged after the reaction (half-an-hour using a 400 W medium-pressure mercury arc) we may conclude that the reactions which occur are fairly efficient.

The second fraction was a mixture which contained N-methylphthalimide (the ^1H -NMR spectrum shows a singlet at $\delta 3.15$, and the ^{13}C -NMR and infrared spectra both show strong absorptions which may be attributed to N-methylphthalimide). The third, fourth, fifth and sixth fractions were all mixtures of products. The fourth fraction showed two doublets in the ^1H -NMR spectrum at $\delta 3.80$ and $\delta 3.55$ ($J = 22$ Hz), which may possibly arise from a methylene group derived from the methyl group of a toluene molecule, as might be expected in reduction

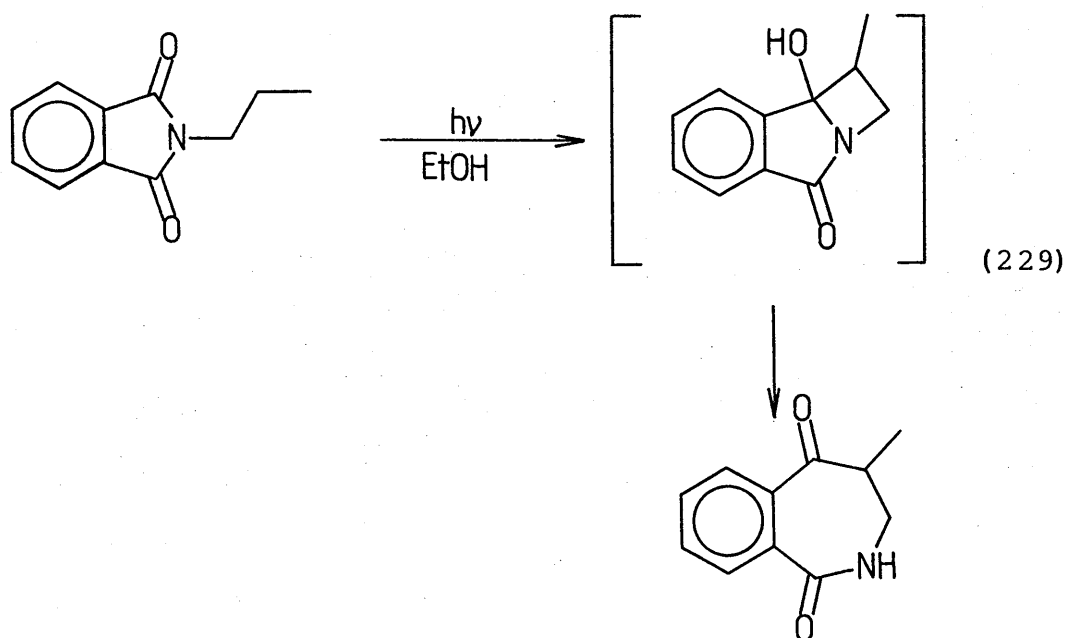
products such as (224). Such products may be proposed by analogy with the reactions of N-methylphthalimide (225)¹⁸ and di-t-butyl thioketone with toluene (226)¹⁴¹, or ethers (227).¹⁴²



Of greater interest are reactions that may lead to cyclised products by way of intramolecular hydrogen abstraction. The choice of N-isobutylthiophthalimide (228) as a substrate was based on it having a methine hydrogen atom at the γ -position; a radical formed by abstraction of this hydrogen atom would be stabilised (it would be a tertiary alkyl radical). The other reason for irradiating this compound was to draw a parallel with the efficient reaction which takes place for N-propylphthalimide²³, in which abstraction of a less highly activated hydrogen atom leads to the formation of a benzazepinedione via an intermediate fused azetidinol (229).



(228)



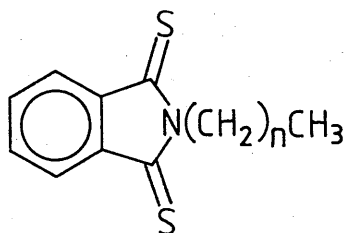
(229)

Irradiation of N-isobutylthiophthalimide (228) was carried out twice, using different wavelength ranges. The first irradiation involved excitation into the $S_0 \rightarrow S_1$ (n, π^*) absorption band, which was achieved by using a high-pressure mercury arc and a $\text{CuCl}_2/\text{CaCl}_2/\text{HCl}$ filter solution, which cut out wavelengths shorter than 475 nm approximately; these reaction conditions would also have led to some absorption into the lowest triplet band (see Chapter Four). The second irradiation involved excitation into both the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ absorption bands, by using a medium-pressure mercury arc with a Pyrex filter, which gives strong emission lines at 313, 366, 405, 440 and 450 nm. The $S_0 \rightarrow S_2$ absorption band of the thiophthalimide, which has a maximum at 329.5, is intense at 313 and 366 nm; the absorption coefficient for the $S_0 \rightarrow S_1$ absorption band is much weaker (see Chapter Four), and so although the mercury emission lines at 440 and 540 nm are as strong as that at 313 nm, and about one-half to two-thirds as strong as that at 366 nm, it would be expected that there would have been much less absorption into S_1 than into S_2 under these experimental conditions of concentration and pathlength.

Neither irradiation led to any products other than the oxidation product, N-isobutylphthalimide (confirmed by running the reaction in the presence of oxygen for a few hours in order to observe the dramatic increase in the relative intensity of the product absorptions as seen in the ^1H -NMR spectrum). This suggests that intramolecular hydrogen abstraction in N-alkylthiophthalimides is not efficient in forming products; the other conclusion which may be drawn is that it seems unlikely that any reaction is occurring from the S_2 state. For the arylalkyl thiones²⁴⁰ the S_2 state shows abstraction of non-activated δ -hydrogen atoms to form

products. The lack of product formation for N-isobutylthiophthalimide following excitation to either S_2 or S_1 , together with the photophysical data for N-methylthiophthalimide (Chapter Four) in which the same emission is seen following excitation to S_2 or to S_1 , would suggest that decay of the S_2 state to the S_1 state is faster than hydrogen abstraction.

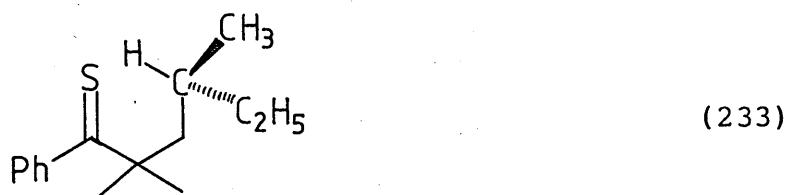
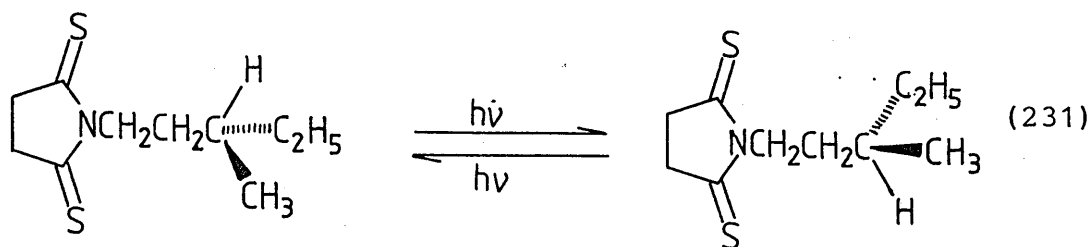
The lack of product formation for N-isobutylthiophthalimide (228) is in keeping with Kanaoka's recent report¹¹⁰ that N-alkyldithiophthalimides (230) are recovered unchanged following irradiation.



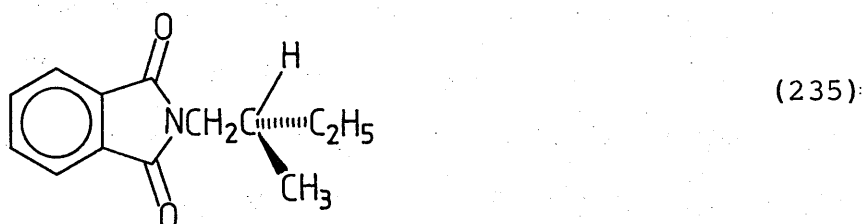
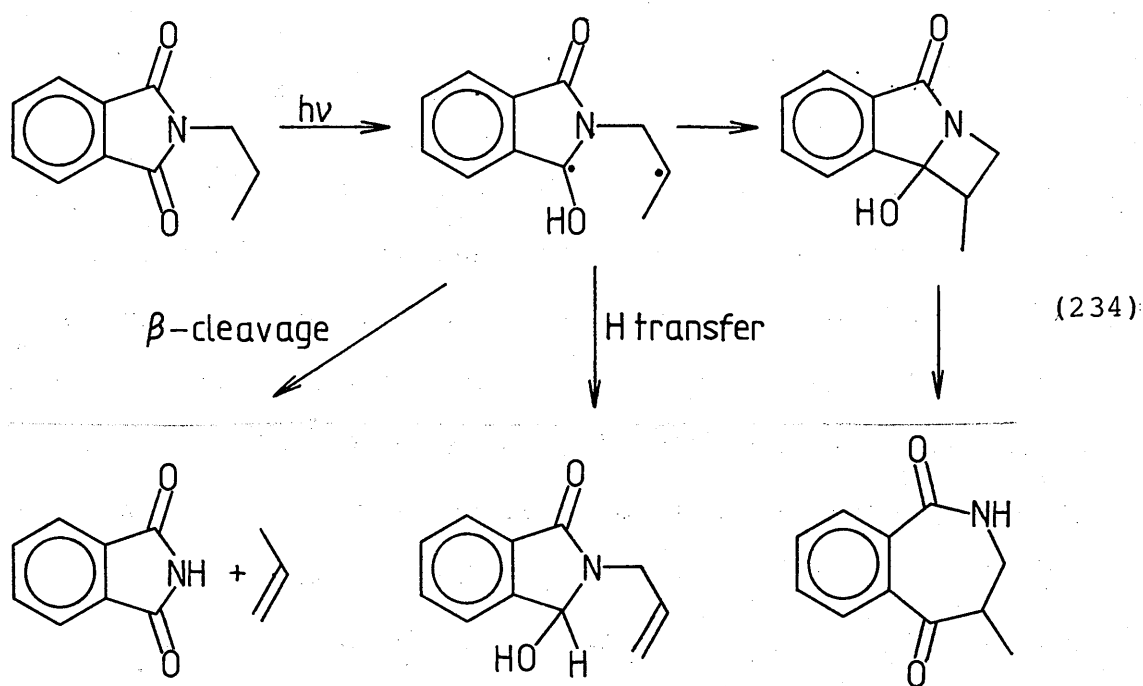
(230)

$$n=1,2,3$$

A similar lack of reactivity was reported for N-alkyldithiosuccinimides in which there were no activated hydrogen atoms. However the irradiation of two chiral molecules (231) and (232) led to racemisation of that with the activated hydrogen in the δ -position (231), but not of that with the activated hydrogen in the γ -position (232). However, no other products were observed, and so it may be concluded that disproportionation to the starting material is a more favourable route for the biradical than cyclisation to form products. By contrast, de Mayo²⁴⁰ saw racemisation for an optically-active arylalkyl thione with an activated γ -hydrogen (233); this latter reaction is known to occur from the triplet state.



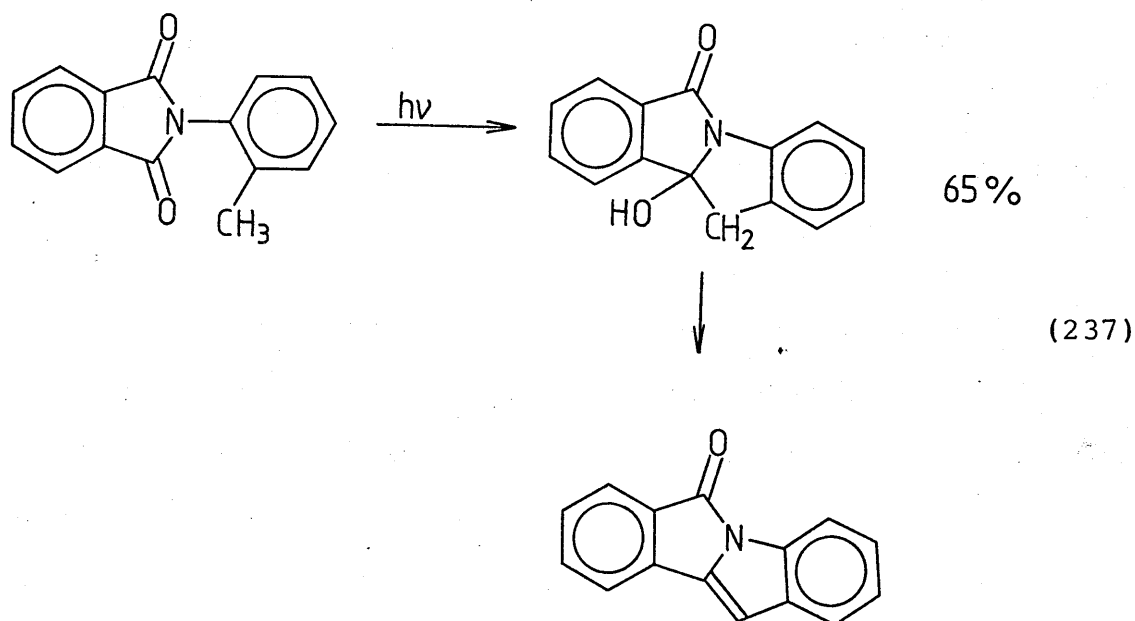
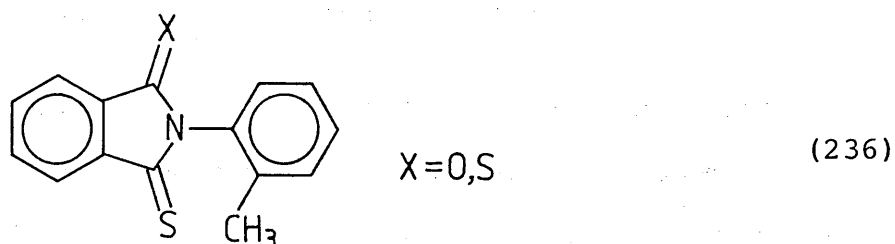
In the case of N-alkylphthalimides the hydrogen transfer reaction takes place at the γ -position to yield various products (234)² (for alcohol solvents, only the benzazepinedione product is isolated). This reaction occurs from the singlet state and probably proceeds through a short-lived intermediate as shown by the non-racemisation of an optically-active N-alkylphthalimide (235).



It is possible that for N-isobutylthiophthalimide reversible hydrogen abstraction of the tertiary hydrogen atom is occurring; a racemisation study on a chiral analogue would be required to investigate this further. It would seem, from a consideration of the energies involved, that hydrogen abstraction of an activated hydrogen atom may not be ruled out on energetic grounds. If the excited state energy of N-isobutylthiophthalimide is comparable with that of the emitting state of N-methylthiophthalimide (Chapter Four) which is 216 kJ mol^{-1} , or the triplet state of N-methyldithiophthalimide, which is 182 kJ mol^{-1} , then it is of comparable magnitude to the triplet energies of the arylalkyl thiones⁹⁸, for which the triplet energies are of the order of 184 kJ mol^{-1} . These latter are known to undergo abstraction of similarly activated γ -hydrogen atoms (233).²⁴⁰

However, this is only a part of the energetic explanation, since other factors such as geometric strain energies and radical stabilisation energies also need to be taken into consideration.

Another two compounds which appeared to be potentially interesting for hydrogen abstraction reactions were the N-o-tolylthiophthalimides (236). These were of interest for comparison with the N-o-tolylphthalimides, for which there is an efficient δ -hydrogen abstraction followed by cyclisation to an alcohol which may be readily dehydrated to the indole derivative (237).¹³



UNRESTRICTED

PHOTOCHEMISTRY OF THIOPHTHALIMIDES

A THESIS SUBMITTED BY

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A CANDIDATE FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

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OPEN UNIVERSITY

VOL II

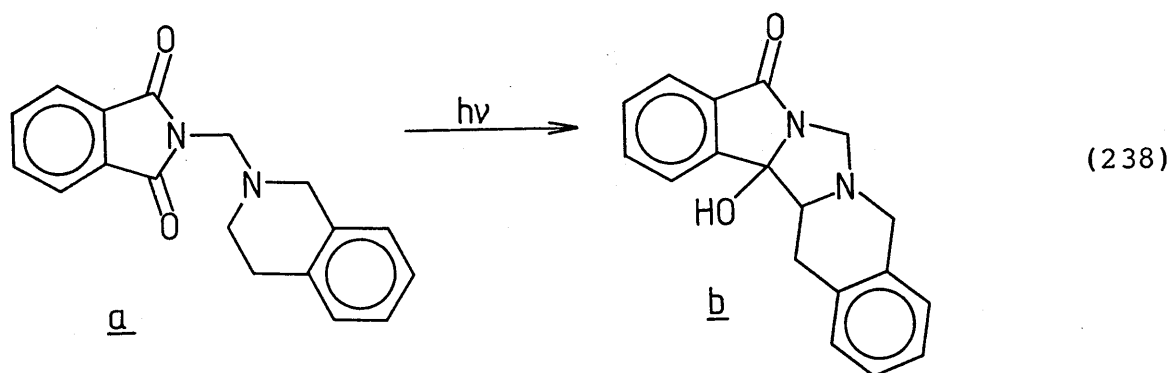
FEBRUARY 1986

Date of Submission: 1.2.86
Date of Award: 16.4.86

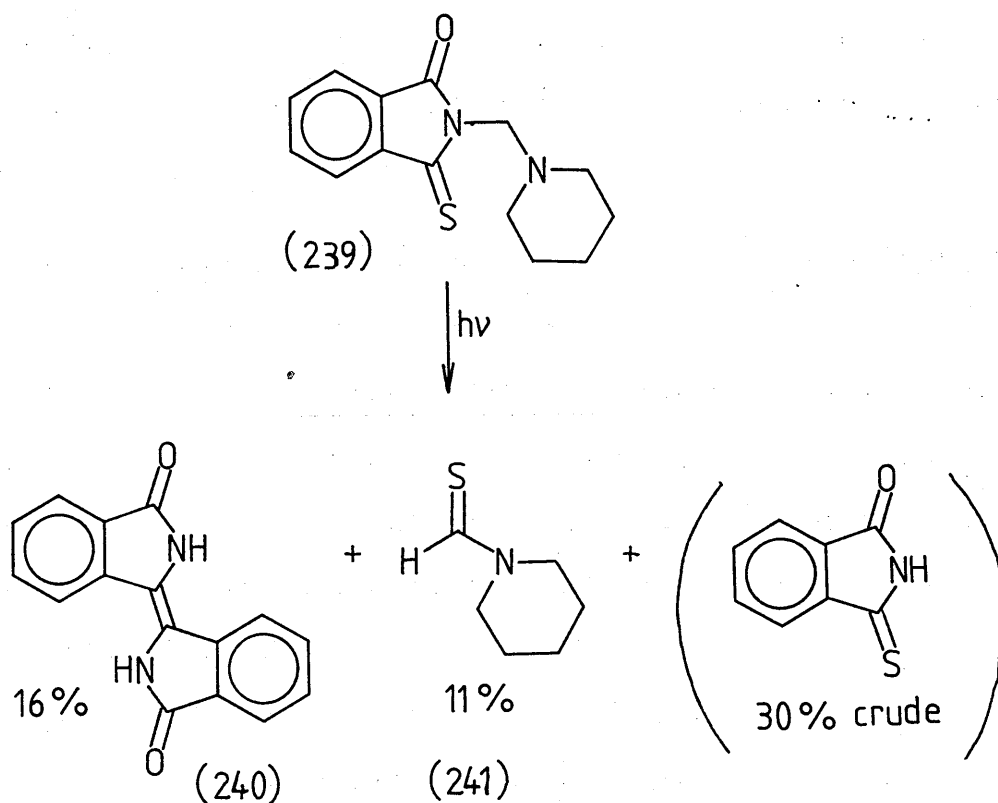
For N-o-tolylthiophthalimide (236, X=O) there is no product formation (other than small amounts of oxidation products) following excitation either to S_1 only, or to S_1 and S_2 , as described for N-isobutylthiophthalimide. (The maxima and absorption coefficients are given in Chapter Four.) As for N-isobutylthiophthalimide it seems likely that excitation to S_2 is followed by fast internal conversion to S_1 . There is no intramolecular thiocarbonyl reaction for comparison, but comparison with N-o-tolylphthalimide shows that whereas the latter has an excited state energy¹³ of the order of 280 kJ mol^{-1} , N-o-tolylthiophthalimide might be expected to have a lower excited state energy; the S_1 energy of N-o-tolylthiophthalimide is 236 kJ mol^{-1} (Chapter Four). N-o-Tolylphthalimide may also react by a different mechanism. Comparison of the reaction of N-o-tolylthiophthalimide with that of N-methylthiophthalimide and toluene suggests that there may be sufficient energy for a similar reaction to occur, but for N-o-tolylthiophthalimide there are also geometric strain factors to be considered. It is not possible to tell whether or not reversible hydrogen abstraction is occurring for N-o-tolylthiophthalimide.

For N-o-tolylldithiophthalimide (236, X=S) the experiment was carried out with excitation into the S_1 band (i.e. using a high-pressure mercury arc with a $\text{CuCl}_2/\text{CaCl}_2/\text{HCl}$ filter solution to cut off wavelengths shorter than 475 nm approximately, and to allow absorption into the $S_0 \rightarrow S_1(n, \pi^*)$ band, for which the maximum is at 526 nm). This was seen to lead only to oxidation products, since all of the product fractions from the chromatography column showed strong carbonyl absorptions in the infrared spectrum.

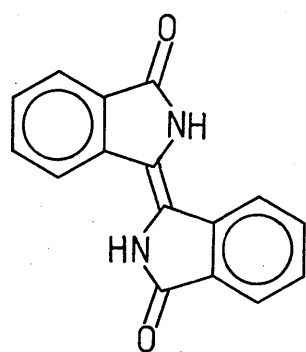
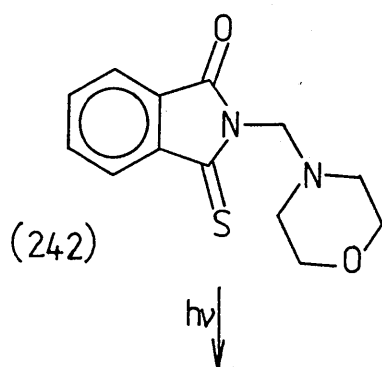
The reported cyclisation reactions of phthalimide Mannich bases^{5,9,32-34} led us to investigate the photochemistry of thiophthalimide Mannich bases. The phthalimide Mannich bases undergo efficient cyclisation reactions (e.g. 238) which are thought to proceed⁹ either by "conventional" hydrogen transfer, or by electron transfer followed by proton transfer.



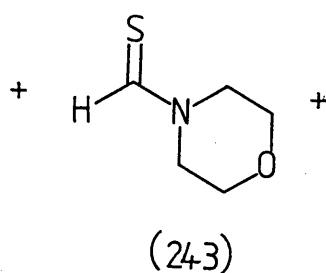
By contrast the thiophthalimide Mannich bases in our study yielded some unexpected cleavage products. N-(Piperidin-1-ylmethyl)thiophthalimide (239) gave β -isoindigo (240) and N-(thioformyl)piperidine (241), together with a mixture of other products. Thiophthalimide was also isolated following column chromatography of the reaction mixture, but it is not possible to tell whether this is an irradiation product or whether it arose from the breakdown of unreacted N-(piperidin-1-ylmethyl)thiophthalimide on the silica column.



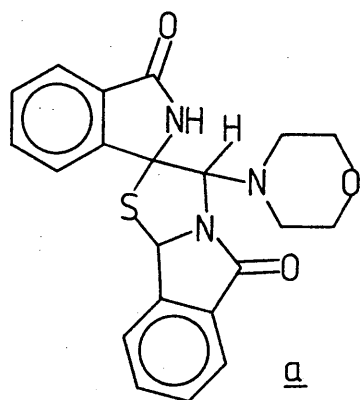
Similarly the irradiation of N-(morpholinomethyl)thiophthalimide (242) yielded β -isoindigo (240), N-(thioformyl)morpholine (243) and a higher molecular weight product (244). In one run of this experiment the oxidation product N-(morpholinomethyl)phthalimide (245) was also formed. A small quantity of thiophthalimide was isolated during another run of this experiment.



(i) 27 %
(ii) 48 %



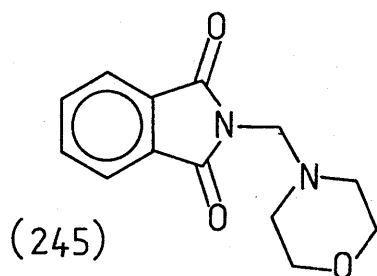
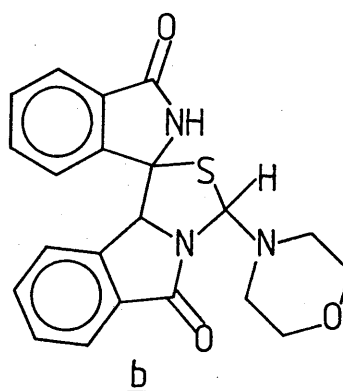
(i) 68 % crude
(ii) 21 % pure



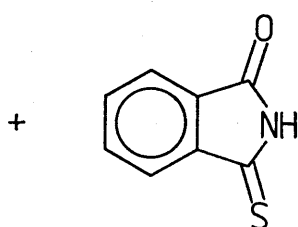
(244)

(i) 1 %
(ii) 7 %

or



(i) 3 %
(ii) 0 %



(i) 0 %
(ii) 2 %

(i) = 1st run
(ii) = 2nd run

The identity of the β -isoindigo product was confirmed by comparison of the infrared spectrum, melting characteristics and solubility characteristics with those of an authentic sample prepared from thiophthalimide and silver using the method of Drew and Kelly.²⁴¹ The structures of the two thioformamide products were confirmed by comparison of their ^1H - and ^{13}C -NMR data with published values²⁴², and for N-(thioformyl)morpholine the mass spectrum was also taken and found to be consistent with the proposed structure: the highest mass ion was at 131.0375, which would be consistent with a parent ion for $\text{C}_5\text{H}_9\text{NOS}$, and the fragment of mass 45 is likely to be a HCS fragment, which would be expected from the proposed structure.

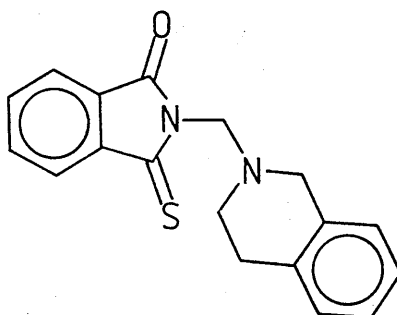
The possible structures (244 a, b) of the higher molecular weight product were deduced from the analytical and spectroscopic data: ^{13}C -NMR showed the presence of twelve aromatic carbon atoms, two carbonyls, one morpholine ring (accounts for 67.0(t) and 48.0(t), showing that the ring is symmetrical), two methine carbon atoms (following off-resonance decoupling seen as 82.9 (d) and 75.5 (d)), and one other quaternary carbon atom (102.7). The infrared spectrum showed two amide carbonyl absorptions, aromatic absorptions and an N-H absorption; ^1H -NMR showed eight aromatic protons, a morpholine ring with unrestricted rotation about the exo-bond on the nitrogen atom (δ 3.80(m,4H), δ 3.15(m,2H) and δ 2.70(m,2H)), two other protons (δ 6.66 and δ 5.65) which appeared as singlets, together with a variable absorption at δ 1.80 which is probably the -NH proton. The CHNS microanalysis was consistent with the empirical formula $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$; in the ordinary mass spectrum the highest mass peak (307) was too low to account for all of the carbon atoms seen in the ^{13}C -NMR spectrum, and so a fast-atom bombardment

mass spectrum was run, which gave a parent ion at 393; this is consistent with the proposed structures. It is not possible to distinguish further between these structures on the basis of the spectral data.

Irradiation of N-(piperidin-1-ylmethyl)thiophthalimide using a high-pressure mercury arc and a filter solution (cut-off ~ 480 nm) gave a complex mixture of products (T.L.C.). Some yellow, insoluble material was seen to have formed (this was retained when the reaction mixture was filtered); a ^1H -NMR spectrum of the reaction mixture showed a singlet at $\delta 9.20$, indicating that N-(thioformyl)piperidine had been formed. Thus, although it is not possible to say that the same reactions are taking place under both types of conditions, some similarities are observed. The high-pressure arc experiment, which gives excitation only into S_1 , suggests that N-(piperidin-1-ylmethyl)thiophthalimide may react from either S_1 or T_1 . Owing to the complexity of the product mixtures it is not possible to see whether any reaction is occurring from S_2 ; however the similarities between the two sets of results indicate that there is some internal conversion from S_2 to S_1 which may compete with direct product formation from S_2 , or which may be so fast that no product formation occurs from the S_2 state.

Irradiation of N-(1,2,3,4-tetrahydroisoquinolin-2-ylmethyl)thiophthalimide (246) in acetonitrile led to an inseparable mixture of products. The yield of β -isoindigo is low (so low that in the first experiment its formation was missed), and the yield of a thioformamide product is also low (<2% as seen by ^1H -NMR; the thioformyl proton is distinct at $\delta 9.45$). A larger fraction (4-5% after some purification) gave IR, ^1H -NMR and ^{13}C -NMR which suggested some kind of cyclised structure.

However mass spectral and microanalytical results indicated that sulphur was not present. It had also been found that this compound tended to decompose easily on heating to yield brown, polymeric products. The spectral results were sufficient to ascertain that this product was neither the oxidation product (238 a) nor one of the diastereoisomers (238 b) which would be expected on irradiation of the oxidation product. The mass spectrum indicated that the isolated material may be a mixture: two spectra run under the same conditions gave slightly different results. One of the components appears to be phthalimide, as indicated by the highest ion value (147, which is M^+ for phthalimide) and the fragmentation pattern, which is consistent with literature results.²⁴³

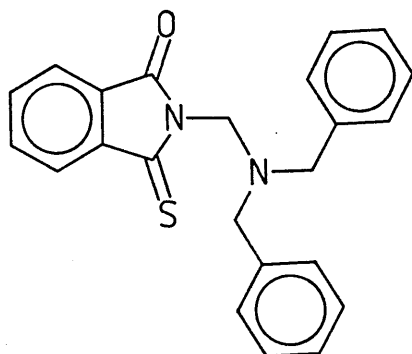


(246)

Irradiation of N-(1,2,3,4-tetrahydroisoquinolin-2-ylmethyl) thiophthalimide in benzene using a medium-pressure mercury arc led to a multi-component mixture of products (T.L.C.) Comparison of this T.L.C. pattern with that from the acetonitrile reaction showed a similar distribution of products.

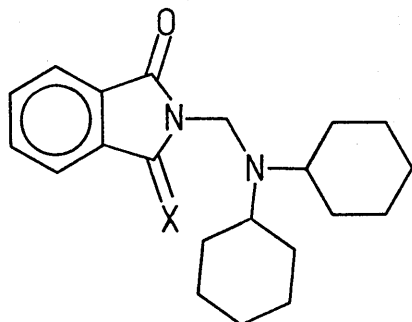
N-(1,2,3,4-Tetraisoquinolin-2-ylmethyl)thiophthalimide was also irradiated using a high-pressure mercury arc. A complex mixture of products (T.L.C. and ^1H -NMR spectrum) was also obtained in this reaction. These results suggest that this Mannich base, like N-(piperidin-1-ylmethyl)thiophthalimide, may react from the S_1 or T_1 states.

Irradiation of N-(dibenzylaminomethyl)thiophthalimide (247) in acetonitrile also led to an inseparable mixture of products. It was noted that no observable quantity of β -isoindigo was formed in this reaction, and no N-(thioformyl)-dibenzylamine was found during the separation of the mixture of products (as seen by $^1\text{H-NMR}$). Irradiation of this same Mannich base in benzene gave similar results to the acetonitrile reaction: the product distribution appeared similar (as seen by T.L.C.), no observable quantity of β -isoindigo was formed, and the product mixture could not be separated to give pure products.



(247)

N-(Dicyclohexylaminomethyl)thiophthalimide (248 a) was irradiated: some β -isoindigo formation was observed, but this reaction was not investigated further in view of the difficulty of obtaining pure products from the reaction mixture (the phthalimide analogue (248 b) similarly formed a complex mixture on irradiation, unlike most phthalimide Mannich bases).

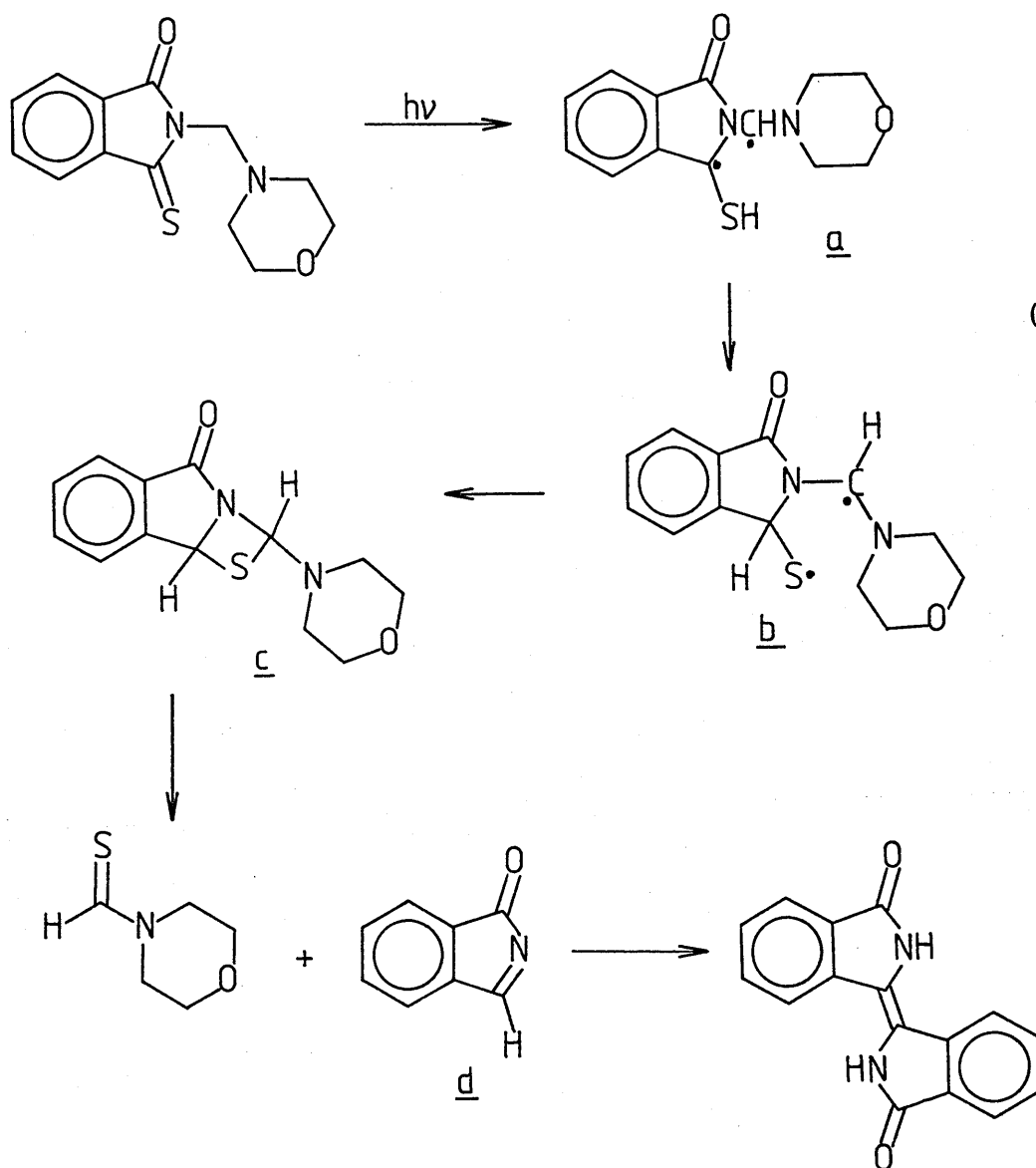


(a) X=S

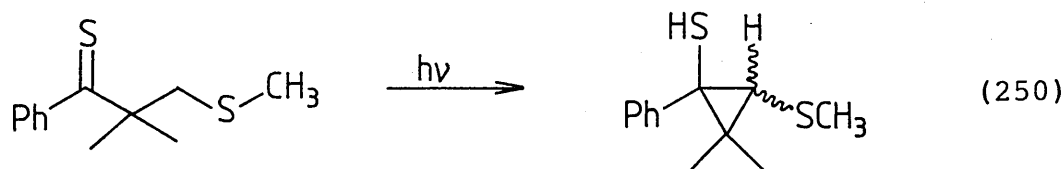
(b) X=O

(248)

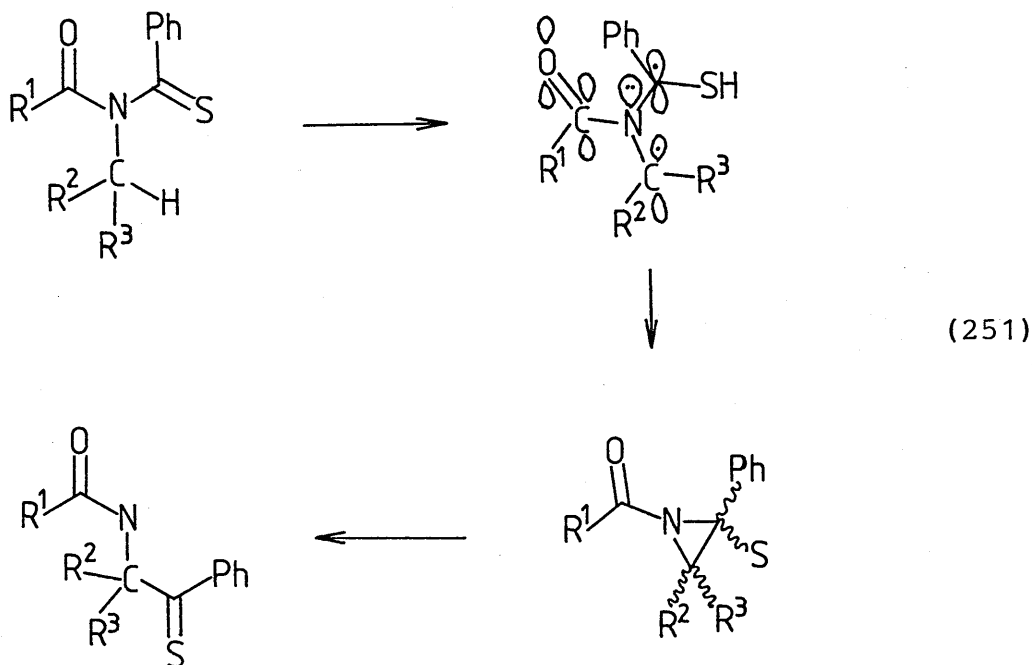
The products isolated from the reactions of the morpholine bases may be accounted for by an initial β -hydrogen abstraction (249). It is likely that the initial hydrogen transfer is to sulphur rather than to carbon; transfer to carbon would be sterically more strained. There could then be a 1,2-hydrogen shift followed by a ring-closure to form a thiazetidine. The thiazetidine may then undergo a reverse cycloaddition reaction to give the thioformamide product together with a molecule of pseudo-isoindolone. The latter dimerises, forming β -isoindigo.

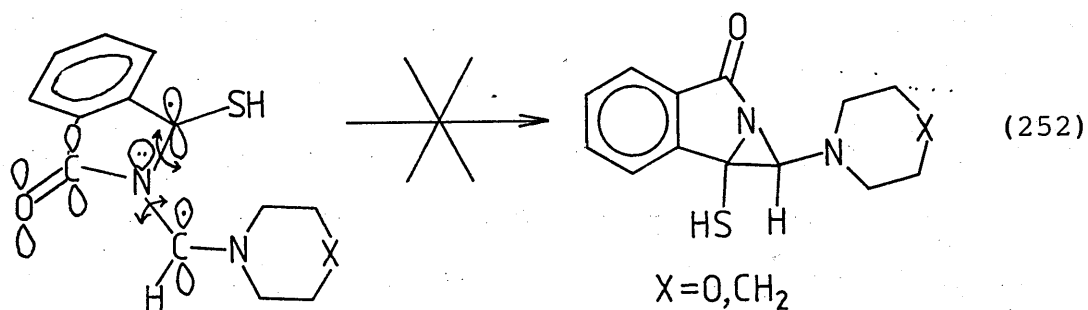


Although both β - and δ -hydrogen atoms are activated by being adjacent to heteroatoms, only β -hydrogen abstraction would account for the observed products. A parallel may be drawn with the irradiation of 3-(methylthio)thiopivalophenone (250) in which the β - and δ -hydrogen atoms are similarly activated, but abstraction occurs at the β -position.¹⁴⁷ This reaction followed excitation to the S_1 state.

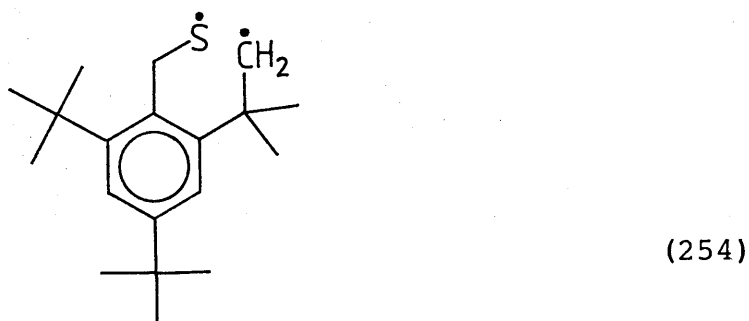
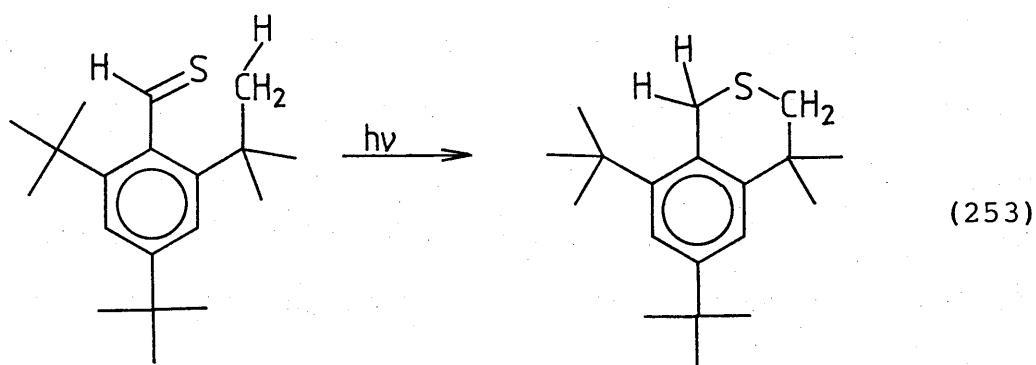


A biradical such as (249 a) would be prevented from forming a cyclopropanethiol, such as occurs for a linear thioimide (251)¹⁸¹, by steric hindrance. The rotation about the isoindole C-N bond which would be necessary for ring closure is geometrically strained (252). Therefore a biradical resulting from β -hydrogen abstraction might well lead to other products or disproportionate.

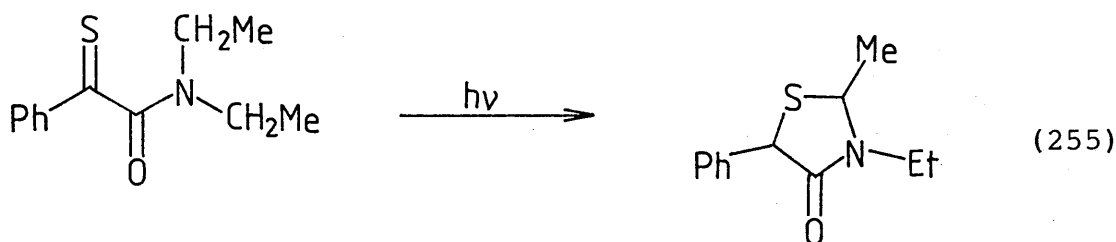




Although no direct evidence exists for the 1,2-hydrogen shift required for transformation of biradical (249 a) into biradical (249 b), there are other thiocarbonyl compounds which show cyclisation to give a product incorporating the sulphur atom into the ring. One such is 2,4,6-tri-t-butylthio-benzaldehyde (253)¹⁵⁷, for which the reaction is known to occur following excitation to the $S_1(n, \pi^*)$ state. However the authors are uncertain whether this reaction is a $[2\pi + 2\sigma]$ concerted reaction, or whether it proceeds via the biradical (254), which would result from a δ -hydrogen abstraction followed by a 1,2-shift.

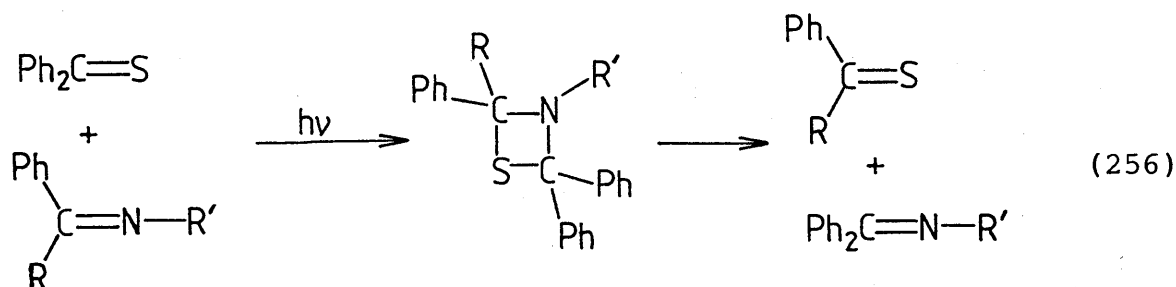


By contrast the other thiocarbonyl compound which shows this cyclisation pattern is an N,N-diethyl- α -thioxoamide (255).¹⁵⁶ This reaction is thought to occur from an upper excited state.



A factor in favour of a 1,2-hydrogen shift occurring for the Mannich bases is that literature examples involving intermolecular hydrogen abstraction have shown that $\text{Ph}_2\text{C}-\dot{\text{S}}$ and $\text{Ph}_2\dot{\text{C}}-\text{SR}$ are not very different in energy.¹³⁸

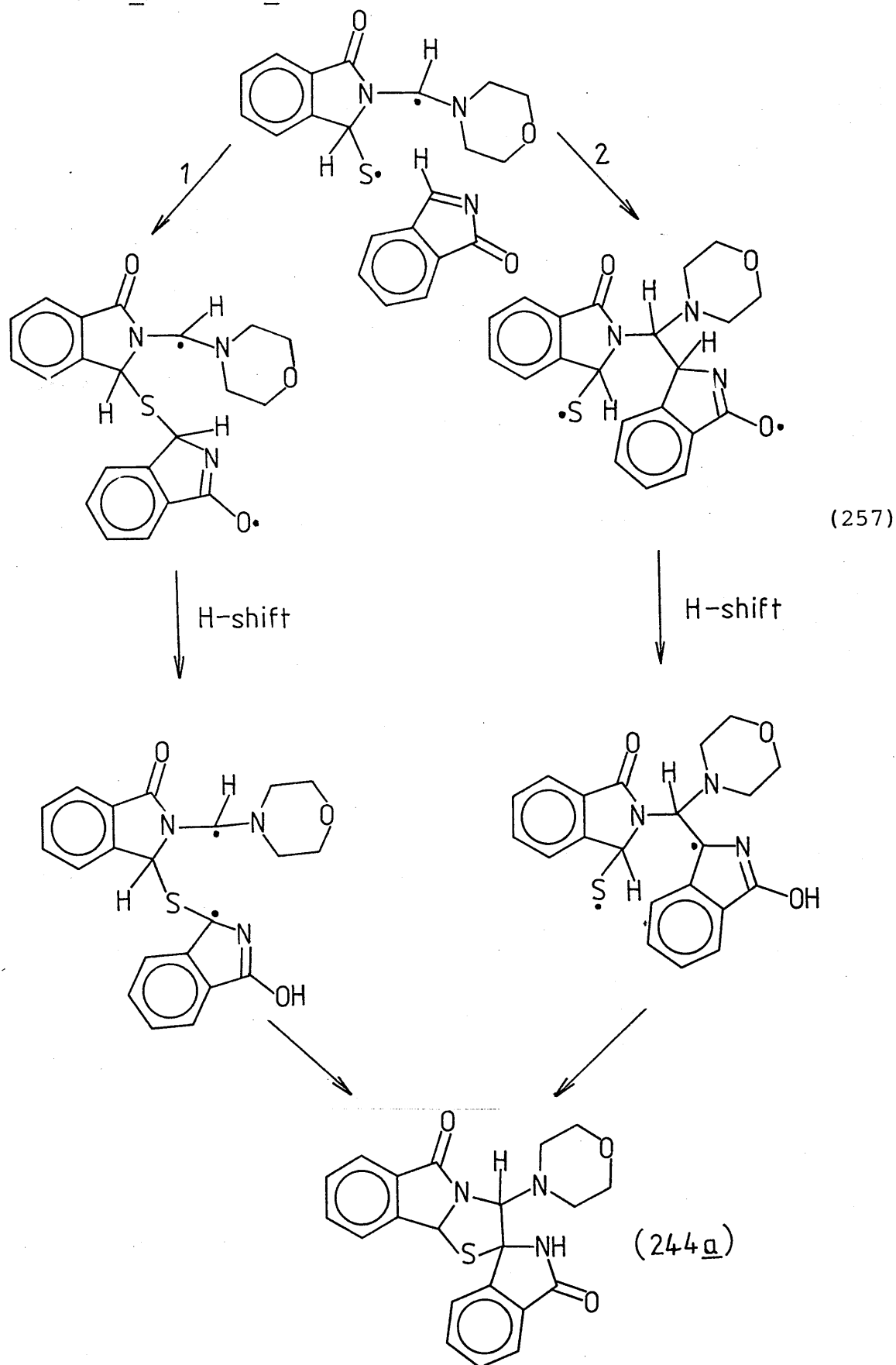
Breakdown of the thiazetidine ring (249 c) has a precedent in that the photocycloaddition reaction of imines with thioketones²¹⁰ leads to products which suggest the formation and cleavage of an intermediate thiazetidine (256).

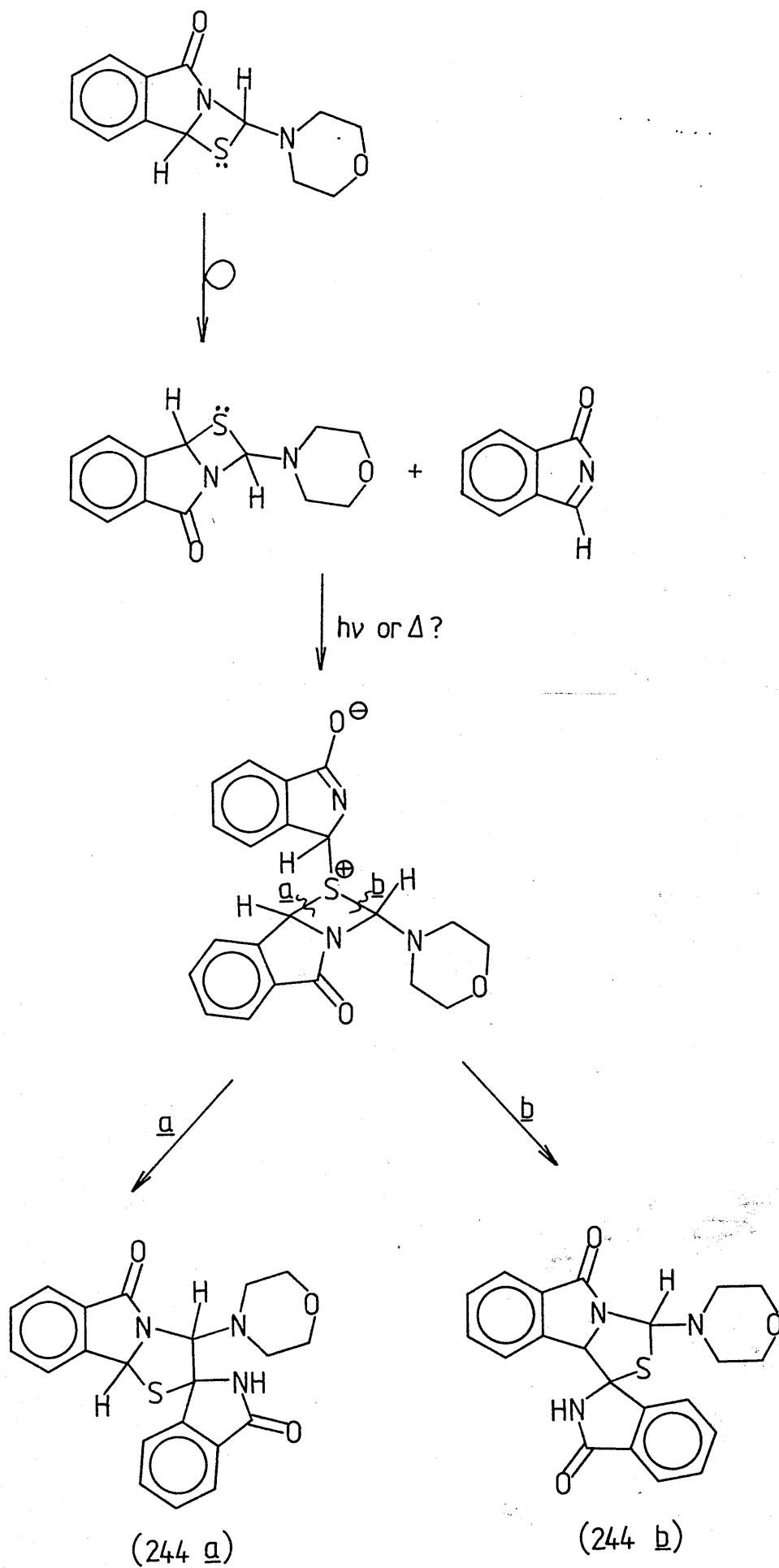


The fact that pseudo-isindolone (249 d) is not isolated as a product comes as no surprise when considering that attempts to synthesise it have resulted in the formation of either β -isindigo or a trimer.²⁴⁴

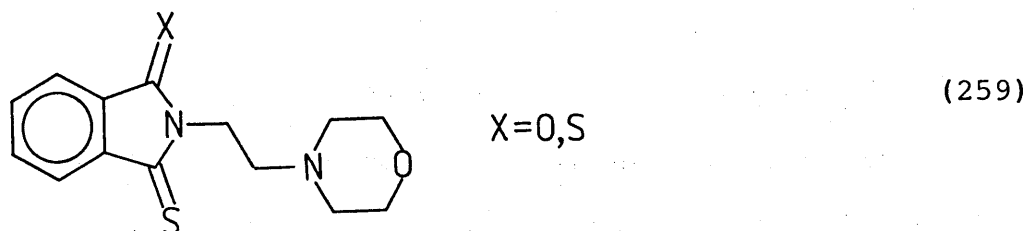
The formation of the additional product (244) from the irradiation of N-(morpholinomethyl)thiophthalimide might be explained in terms of the reaction of one molecule of pseudo-isindolone with either a thiazetidine molecule or a biradical

(249 b). Reaction with the biradical (257) would be unlikely, as both species would be expected to be short-lived, but would lead to product (244 a) only; however, reaction with the azetidine could lead (258) to either (244 a) or (244 b).

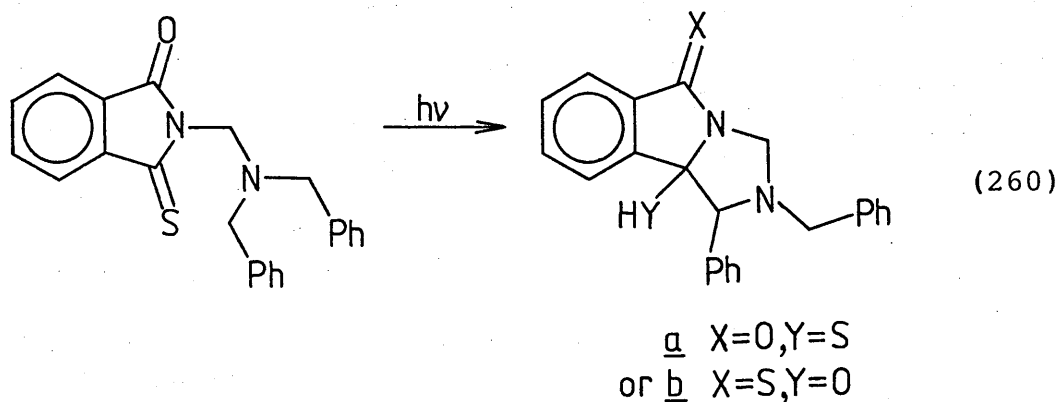


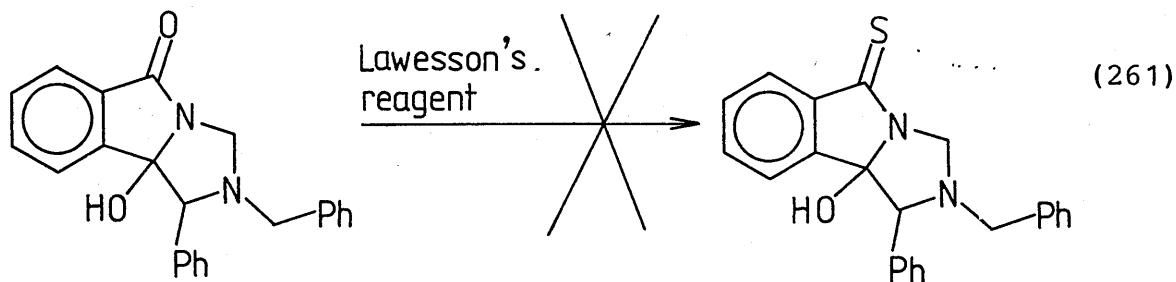


A final system studied in order to extend the range of information about thiophthalimide systems that might undergo intramolecular hydrogen abstraction was the N-(2-morpholinoethyl) thiophthalimides (259). Upon irradiation in acetonitrile solution both of these compounds led to inseparable mixtures of products; there was no major product in either case, nor was any β -isoindigo seen to have formed.



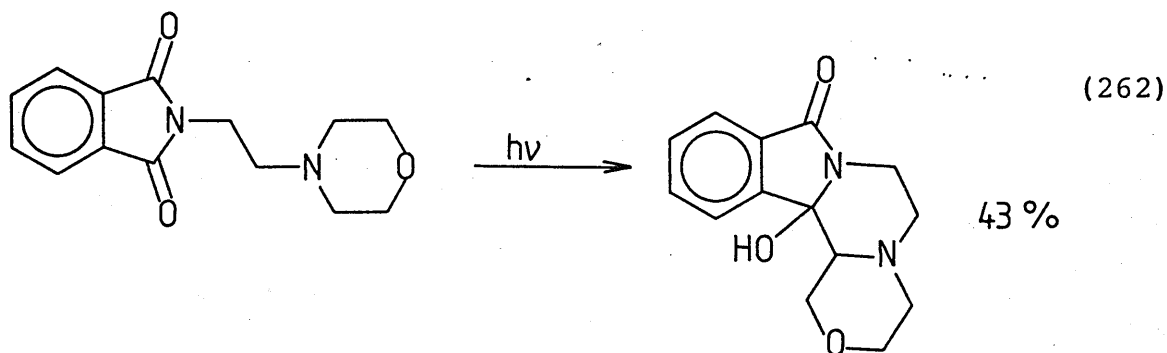
To investigate another route to a product molecule which might be proposed on the basis of a reaction analogous to that for N-(dibenzylaminomethyl)phthalimide (260), we attempted a thiation reaction of the phthalimide Mannich base photoproduct 2-benzyl-9b-hydroxy-1-phenyl-2,3,5,9b-tetrahydro-1H-imidazo-[4,3-a] isoindol-5-one (261).³² Treatment of this compound with Lawesson's reagent led to a mixture of products, all of which showed a carbonyl absorption in the infrared spectrum, and there was no evidence for formation of the thiocarbonyl analogue (260 b); such a compound is one of the products which could, in principle, be formed from a photocyclisation reaction from irradiation of the thiophthalimide Mannich base.



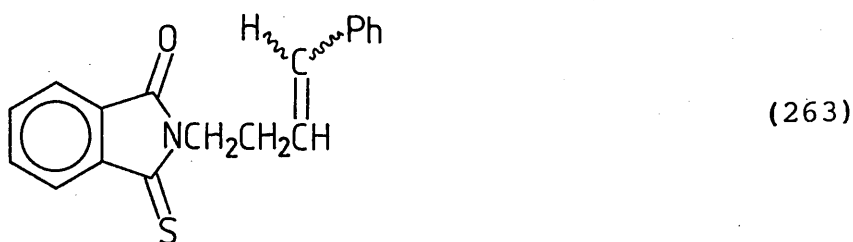


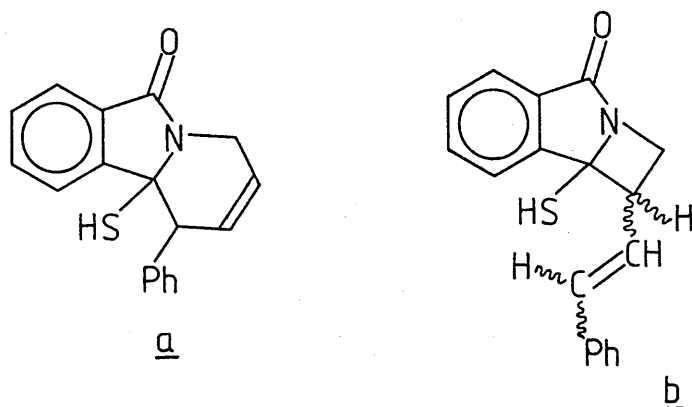
The main conclusion to be drawn from the Mannich base experiments is that there is little evidence for products that might arise by hydrogen abstraction mechanisms similar to those for the related phthalimide systems. Other conclusions are that the formation of β -isoindigo and the substituted thioformamide are favoured in dialkyl Mannich bases (piperidino, morpholino and dicyclohexylamino), but are less favourable in those Mannich bases where there are aryl groups included in the substituents (1,2,3,4-tetrahydroisoquinolin-1-yl and dibenzyl), and that δ -hydrogen abstraction does not appear to be a favourable reaction for the piperidino, morpholino and dicyclohexylamino Mannich bases, as the products which were isolated would be most easily accounted for by an initial β -hydrogen abstraction.

The product mixes yielded by the N-(2-morpholinoethyl)thio-phthalimides show that the processes which occur during the reaction are not identical to those of N-(2-morpholinoethyl)-phthalimide, which reacts to give a product analogous to those obtained from phthalimide Mannich bases (262).²⁴⁵



The photocyclisation reaction of N-(4-phenylbut-3-enyl)-thiophthalimide (263), which was introduced in the preceding chapter, may be explained in terms of a γ -hydrogen abstraction by the thiocarbonyl sulphur atom, followed by ring closure of the biradical; this mechanism was proposed in Chapter Two. There is no evidence for products arising from an initial hydrogen abstraction at the β -position. Preference for abstraction of the γ -hydrogen atom may arise because of the allylic stabilisation afforded to the biradical intermediate. The product structure shows a shift in the position of the double bond with respect to the phenyl group and the nitrogen atom, which would be in accordance with the intermediacy of an allylic biradical. Formation of the six-membered cyclic thiol (264 a) in preference to a four-membered cyclic thiol (264 b) is likely to be because the latter is geometrically strained and sterically crowded. Although such strain does not preclude its formation (many photochemical reactions produce strained four-membered rings), the six-membered ring is more favoured on energetic grounds.



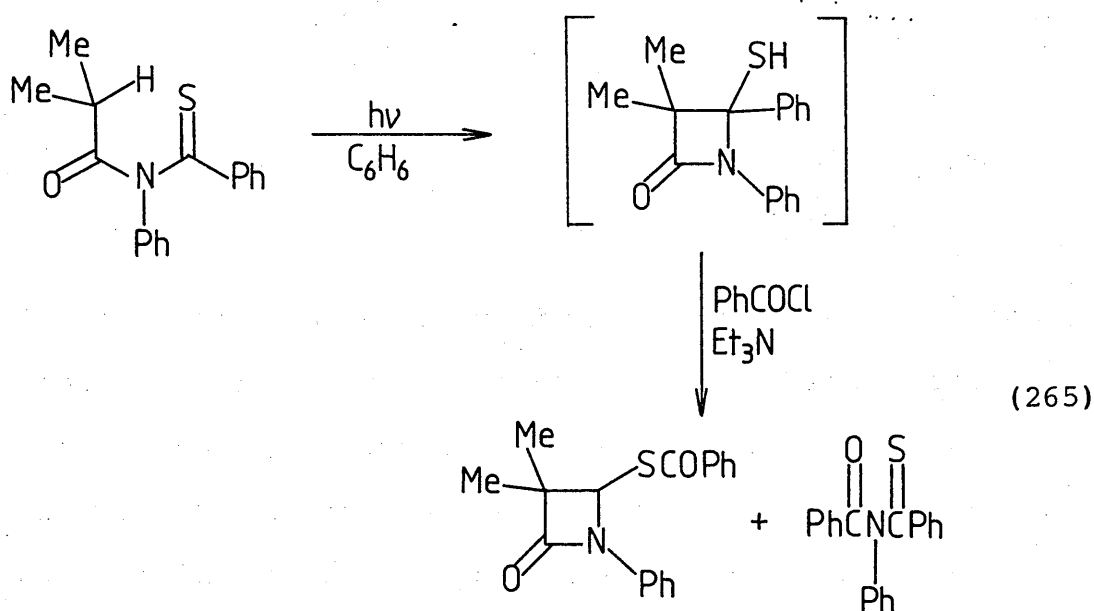


To initiate this reaction the substrate was excited to the $S_1(n, \pi^*)$ state by use of a high-pressure mercury lamp and a filter solution (as described earlier in this Chapter), and thus the reaction probably occurs from either the $S_1(n, \pi^*)$ state or the $T_1(n, \pi^*)$ state.

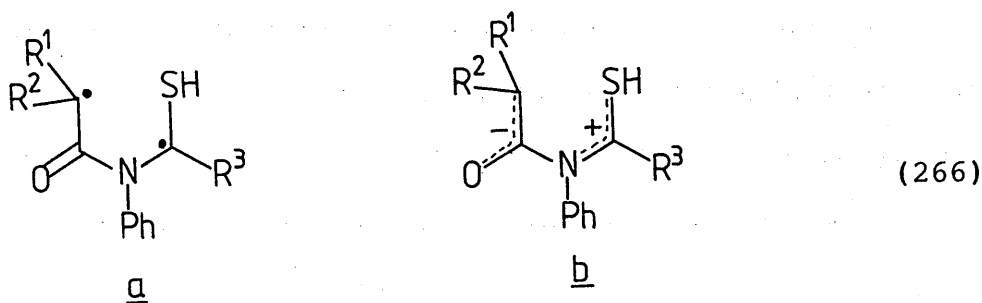
The photocycloaddition reactions of comparable unsaturated compounds, including an α, β -unsaturated thiocarbonyl compound and N-(alkenyl)phthalimides, were discussed in the preceding chapter; these were reported to lead to photocycloaddition products or, in the case of certain N-(alkenyl)phthalimides, solvent incorporation products also.

Other thiocarbonyl systems in which hydrogen abstraction occurs are O-alkyl thiobenzoates,¹⁵⁸⁻¹⁶¹ for which the reaction has been shown to occur from the $^3(n, \pi^*)$ state,⁹³ N-(acyl)-thiazolidine-2-thiones,¹⁶² and some aralkyl thiones in which the γ -hydrogen atom(s) is activated by an adjacent heteroatom; such aralkyl thiones may react from both the S_2 and T_1 states.^{152, 240} N,N-Dialkyl- α -thioxoamides are also reported to give γ -hydrogen abstraction products¹⁵⁶; however it is suggested that these reactions occur from an excited state which is higher in energy than S_1 or T_1 . An acyclic thioimide

has recently been reported²⁴⁶ to react by way of γ -hydrogen abstraction upon irradiation (265).



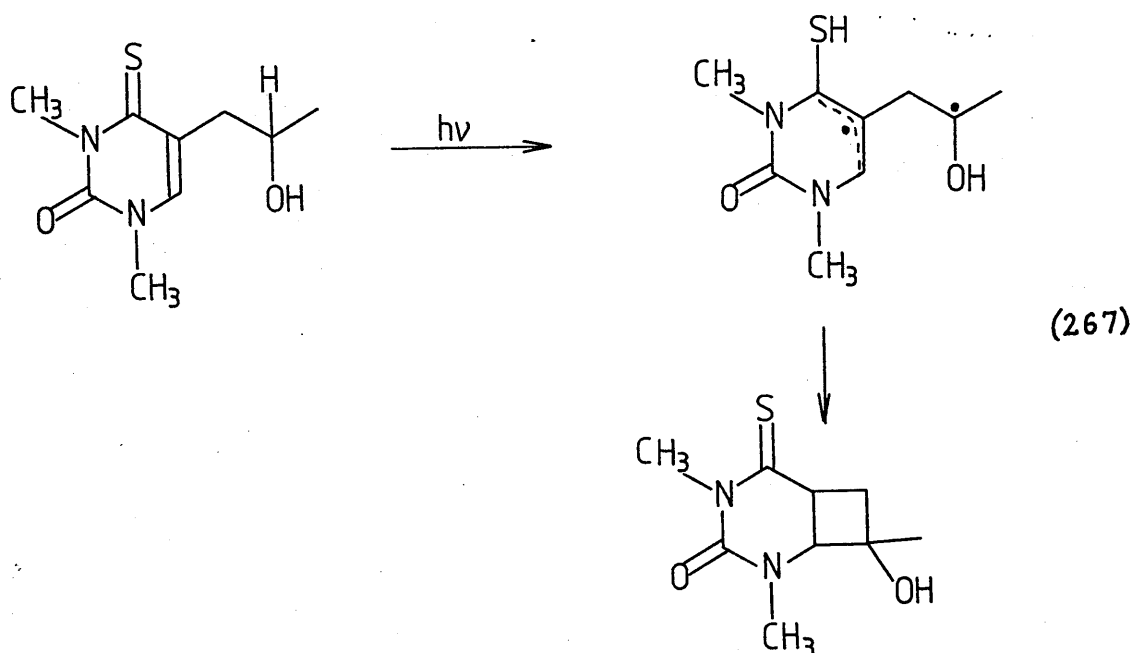
Benzoylation was required to give stable products. The intermediates for these reactions are postulated to be either biradicals (266 a) or zwitterions (266 b).



However these systems are non-rigid, and therefore they do not provide a close comparison for the thiophthalimide system.

A better system for comparison is provided by the photocyclisation reactions of 5-hydroxypropyl-4-thiouracil derivatives.¹⁵⁵ The similarity to our system arises from the abstraction of an activated (in this case by an adjacent OH group) γ -hydrogen atom from the side chain of a rigid system which incorporates the thiocarbonyl group. The authors suggest that the reaction occurs from an (n, π^*) state even though the

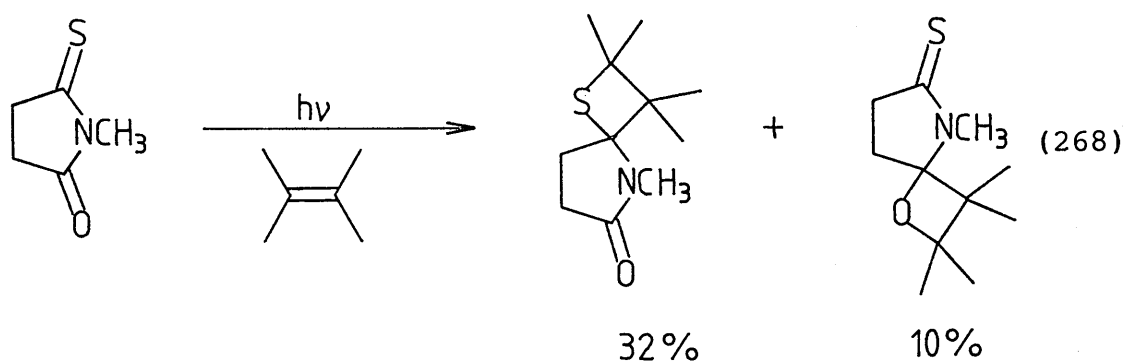
initial excitation is to a (π, π^*) state, and propose a 1,4-biradical as the most likely intermediate (267).



There is no intramolecular photochemical reaction of a phthalimide with which the reaction of N-(4-phenylbut-3-enyl)-thiophthalimide is directly comparable. An intermolecular analogy arises in the reaction of N-methylphthalimide with cyclohexene, giving rise to an alcohol product which might be formed by abstraction of a hydrogen atom from a position adjacent to a double bond (9).¹⁹ However it is possible that this reaction may take place via a different mechanism (electron transfer followed by proton transfer), and it is also rather inefficient on account of a competing photocycloaddition reaction.

One feature which has emerged from both the photocycloaddition and hydrogen abstraction reactions is the lack of reaction at the carbonyl group in monothiophthalimides: in no case has there been retention of the thiocarbonyl group with loss of the carbonyl group. This observation serves to give some indication about the electronic distribution in the reactive excited state of the thiocarbonyl compound, suggesting

that the electronic distribution around the thiocarbonyl group in the reactive excited state is markedly different from that in the ground state, whereas the electronic distribution around the carbonyl group is little changed. This is in keeping with the photoreactions of other thiocarbonyl compounds in which carbonyl groups are also present, such as thiouracils, thioparabanates and 1,2-thioxoamides; the only instance in which there is reaction at the carbonyl group is for the reaction of N-methylthiosuccinimide with 2,3-dimethylbut-2-ene¹¹⁰, in which the oxetane product is obtained in addition to the thietane (268).



CHAPTER FOUR

PHOTOCHEMISTRY OF THIOPHTHALIMIDES:

PHOTOPHYSICS

RESULTS AND DISCUSSION

Interest in the photophysical properties of thiophthalimides arose from the results of the photochemical reactions; some preliminary investigation into the photophysics was necessary in order to provide part of the basis for proposed mechanisms for the reactions.

The ultraviolet/visible absorption spectra of four N-substituted thiophthalimides were measured in ethanol solution at room temperature and found to be very similar. Figure 4.1 shows the absorption spectrum of N-methylthiophthalimide and Figure 4.2 shows that of N-(piperidin-1-ylmethyl)thiophthalimide. Table 4.1 summarises the results for the four compounds. Further absorption measurements were carried out on N-methylthiophthalimide in different solvents. These results are summarised in Table 4.2.

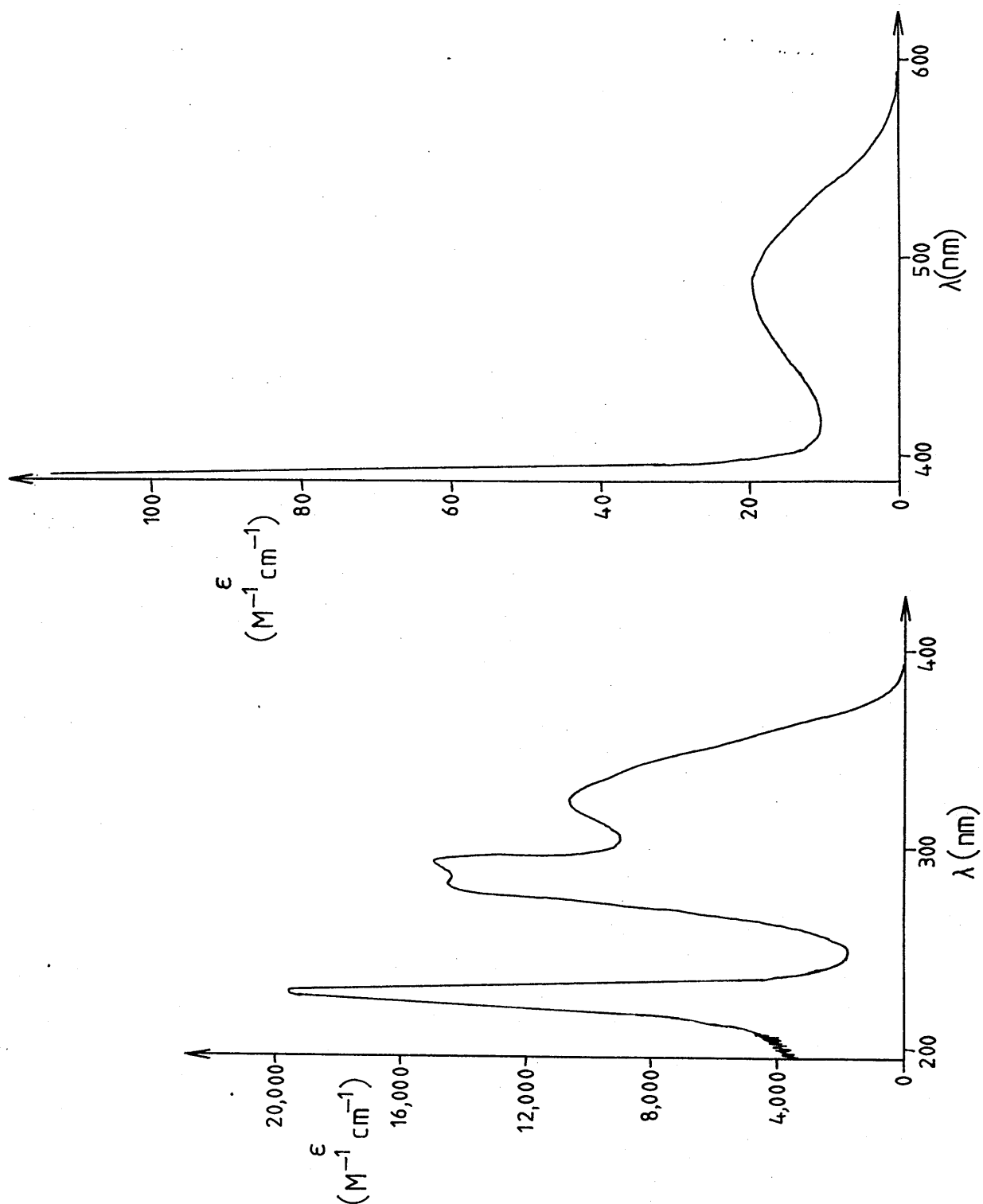


Figure 4.1: The electronic absorption spectrum of
N-methylthiophthalimide

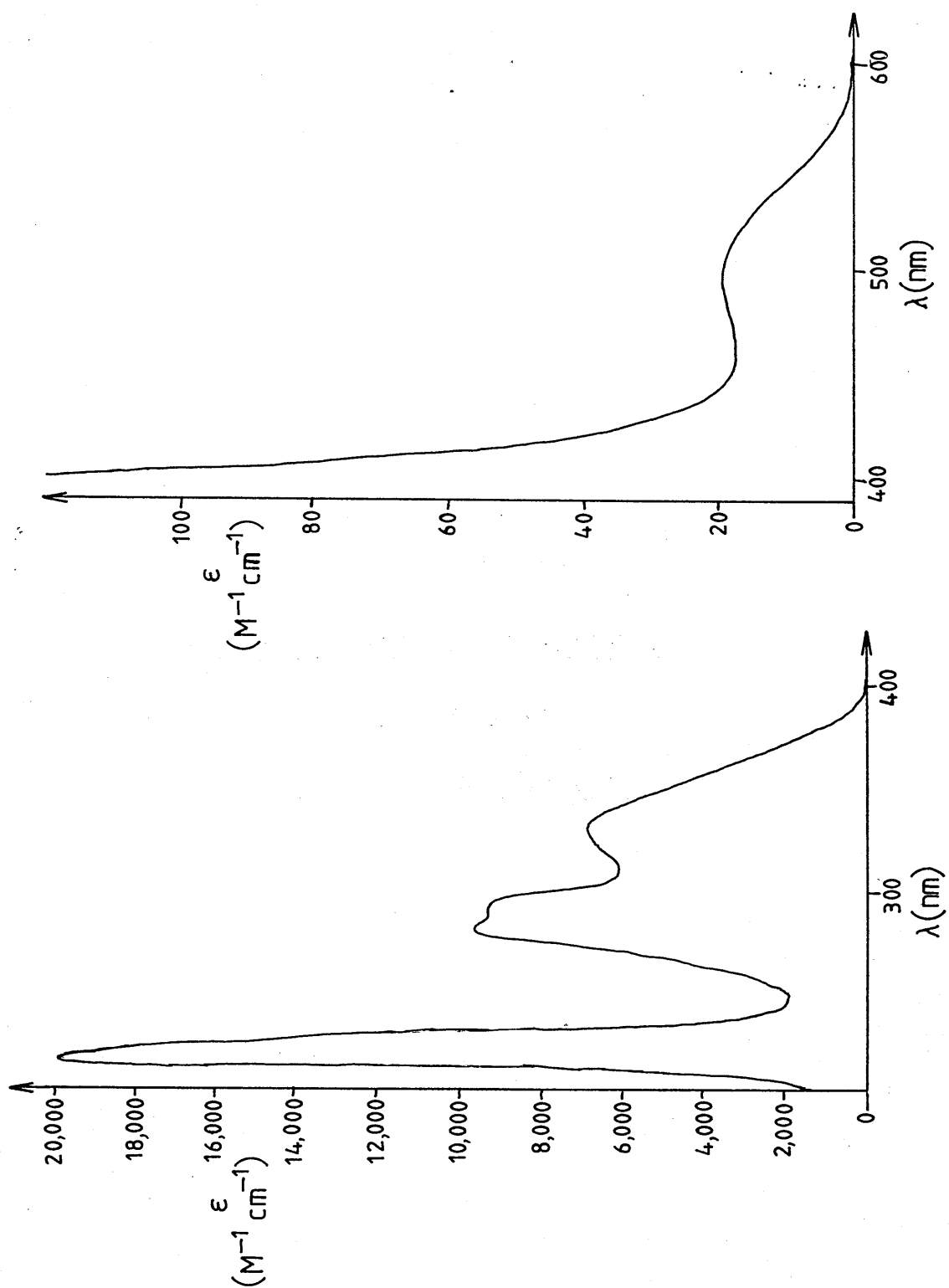


Figure 4.2: The electronic absorption spectrum of *N*-(piperidin-1-ylmethyl)thiophthalimide

Compound	$S_0 \rightarrow S_1$ λ_{\max} (nm) ($1 \text{ mol}^{-1} \text{ cm}^{-1}$) ϵ	$S_0 \rightarrow S_2$ λ_{\max} (nm) ($1 \text{ mol}^{-1} \text{ cm}^{-1}$) ϵ	Third Band λ_{\max} (nm) ($1 \text{ mol}^{-1} \text{ cm}^{-1}$) ϵ	Fourth Band λ_{\max} (nm) ($1 \text{ mol}^{-1} \text{ cm}^{-1}$) ϵ
N-Methylthiophthalimide	489 20	328.5 10,500	297 14,800	232 19,400
N-O-Tolylthiophthalimide	506 18	329 8,550	298 11,400	233.5 32,100
N-Isobutylthiophthalimide	493.5 19	329.5 6,860	298.5 9,660	235.5 20,600
N-(Piperidin-1-ylmethyl)-thiophthalimide	499 21	329 5,300	297.5 7,060 290 7,240	231 12,000

Table 4.1: Electronic absorption characteristics of some N-substituted thiophthalimides in ethanol solution.

Solvent	Dielectric constant ²⁴⁷ at 25 °C	$S_0 \rightarrow S_1$ λ_{\max} (nm) ($1 \text{ mol}^{-1} \text{ cm}^{-1}$) ϵ	$S_0 \rightarrow S_2$ λ_{\max} (nm) ($1 \text{ mol}^{-1} \text{ cm}^{-1}$) ϵ	Third band λ_{\max} (nm) ($1 \text{ mol}^{-1} \text{ cm}^{-1}$) ϵ	Fourth band λ_{\max} (nm) ($1 \text{ mol}^{-1} \text{ cm}^{-1}$) ϵ
Dichloromethane	0.89	488 23	not measured	†	†
Methylcyclohexane	2.02*	494 23	327 9,480	297 13,200 287.5 12,800	230.5 21,500
Benzene	2.28	490 25	not measured	†	†
Ethanol	24.58	489 20	328.5 10,500	297 14,800	232 19,400
Acetonitrile	37.50*	484 34	328 10,400	296 14,600	234 19,900

* = at 20 °C

† = not measured because of solvent absorption in this region.

Table 4.2: Solvent effects on the electronic absorption characteristics of N-methylthiophthalimide

The main conclusion which can be drawn from the data in Table 4.1 is that all of the N-substituted thiophthalimides resemble N-methylthiophthalimide in their absorption characteristics, except for slight differences in the position of the $S_0 \rightarrow S_1$ maximum and in the absorption coefficients. These are to be expected, as the substitution patterns around the nitrogen atom will cause different ordering of solvent molecules around the thioimide moiety and hence different thermodynamic parameters associated with solvation. This effect also accounts for the shift in the absorption maximum with solvent polarity for excitation to the S_1 state, as shown in Table 4.2; the wavelength of maximum absorption correlates qualitatively with dielectric constant, except for dichloromethane (it is not clear why this should be so, although it has also been observed^{73(c)} to be the case for some thioketones). Such a shift of absorption maximum with solvent polarity leads us to assign the S_1 state as (n, π^*) .²⁴⁸ From these results it is not possible to assign the S_2 state with certainty although, from the absorption coefficient values, from considerations of energy levels in the ground state, and by comparison with N-methylphthalimide⁹ and with other thiocarbonyl compounds⁶⁴ it might seem likely that this is a (π, π^*) state. No definite assignment can be made for the third and higher bands.

It is noticeable that there are no apparent charge-transfer bands in the spectrum of N-o-tolylthiophthalimide. However for N-(piperidin-1-ylmethyl)thiophthalimide the absorbance observed between the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ bands is slightly greater than that observed in the comparable spectrum of N-methylthiophthalimide (Figures 4.1 and 4.2). A similar effect is seen when comparing the spectrum of a mixture of cis- and trans-N-(4-phenylbut-3-enyl)thiophthalimides in

chloroform solution with that of a chloroform solution of N-methylthiophthalimide. However it is not clear whether these observed increases in absorption correspond to excited charge-transfer states of low energy.

As is clear from Figures 4.1 and 4.2, the spectra are not sharply resolved; in most solvents the vibrational progression of the $n \rightarrow \pi^*$ transition cannot be observed, and there is only a Frank-Condon envelope. However in methylcyclohexane a series of vibrational bands can be distinguished as described in Table 4.3.

λ_{max} (nm)	437	463	493	515	526
Wavenumber (cm^{-1})	22,880	21,600	20,280	19,420	19,010
Wavenumber differences (cm^{-1})	1280	1320	860	410	
			1270		

Table 4.3: Vibrational fine structure in the ($n \rightarrow \pi^*$) absorption of N-methylthiophthalimide

The vibrational progression would be expected to be around $1,000 - 1,300 \text{ cm}^{-1}$ in view of the infrared absorption values of ground-state thiocarbonyl compounds. An infrared spectrum of N-methylthiophthalimide in tetrachloromethane solution (methylcyclohexane is an unsuitable solvent for solution infrared spectra) shows strong absorptions at $1,075 \text{ cm}^{-1}$, $1,134 \text{ cm}^{-1}$ and $1,323 \text{ cm}^{-1}$, and medium absorptions at $1,184 \text{ cm}^{-1}$ and $1,215 \text{ cm}^{-1}$, but it is not possible to say which of these is the C=S stretching band.

In addition to the vibrational progression described above, the ($n \rightarrow \pi^*$) absorption of N-methylthiophthalimide shows a long tail with a small maximum at 553 nm, for which the absorption coefficient is $6 \text{ l mol}^{-1} \text{ cm}^{-1}$. This is shown

in Figure 4.3. This absorption does not appear to be part of the vibrational progression (553 nm corresponds to $18,100\text{ cm}^{-1}$, a difference of 910 cm^{-1} from the last entry in Table 4.3).

It is possible that this may be a $S_0 \rightarrow T_1$ absorption, as has been reported for some thioketones⁸¹, such as thiobenzophenone, thiofenchone and thiochloestanonone, where the absorption coefficients range from 2 (for thiofenchone) to 89 (for thio-benzophenone).

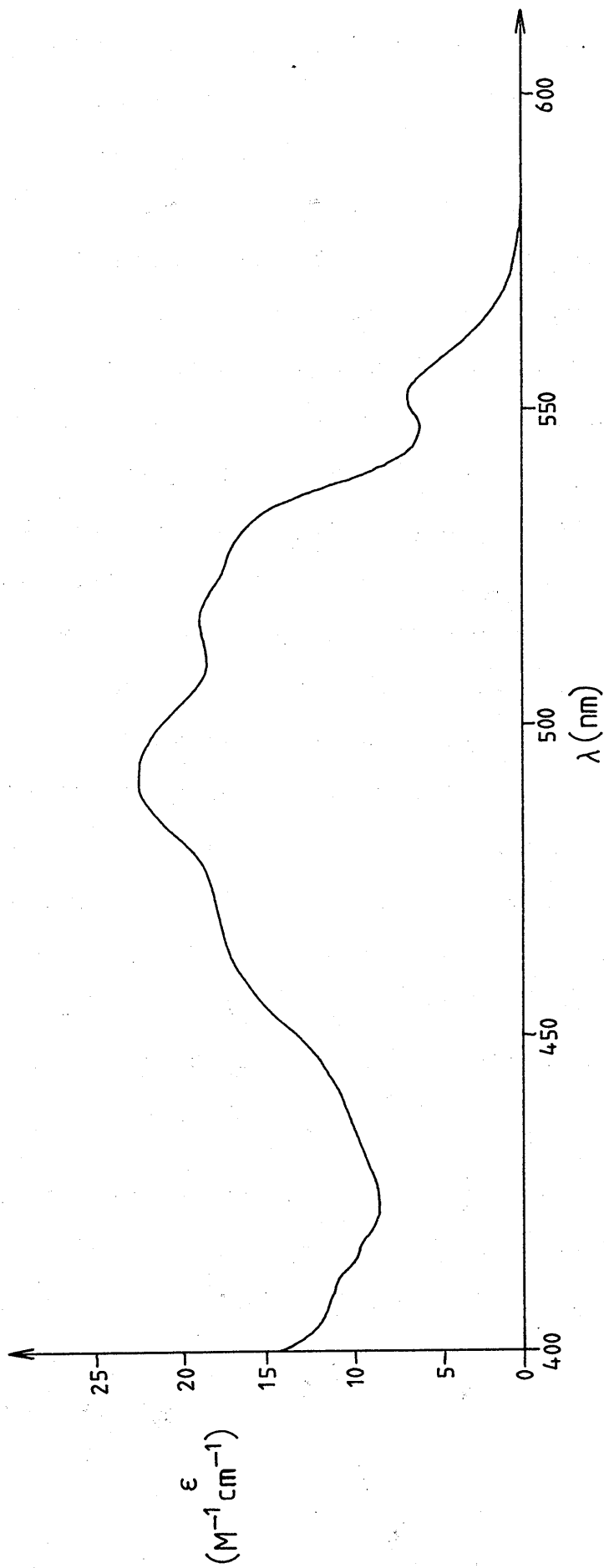


Figure 5.4: The ($n \rightarrow \pi^*$) absorption band for N-methylthiophthalimide in methylcyclohexane

The electronic absorption spectra of some N-substituted dithiophthalimides have also been investigated, although less extensively. A comparison of the room temperature spectra of N-methyldithiophthalimide and N-o-tolyldithiophthalimide in ethanol solution is given in Table 4.4.

N-o-Tolydithiophthalimide also shows a fourth band with λ_{max} at 204 nm, $\epsilon = 27,300 \text{ l mol}^{-1} \text{ cm}^{-1}$. As with the monothiocompounds it can be seen that the two spectra are similar except for the λ_{max} of S_1 . Some solvent studies have been carried out on the electronic absorption of N-methyldithiophthalimide, and the results are summarised in Table 4.5. The results are similar to those for N-methylthiophthalimide in that there is a shift to shorter wavelength for the $S_0 \rightarrow S_1$ band on going from non-polar to polar solvents, and so this band may be assigned as an $(n \rightarrow \pi^*)$ absorption.

Solvent	$S_0 \rightarrow S_1$		$S_0 \rightarrow S_2$		Third band	
	λ_{\max} (nm)	ϵ ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	λ_{\max} (nm)	ϵ ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	λ_{\max} (nm)	ϵ ($l \text{ mol}^{-1} \text{ cm}^{-1}$)
<u>N</u> -Methyldithiophthalimide	491.5	70	356	23,300	245	17,800
<u>N</u> - <u>O</u> -Tolyldithiophthalimide	526	48	358	21,300	246	23,000

Table 4.4: Electronic absorption spectra of N-substituted dithiophthalimides

Solvent	Dielectric constant ²⁴⁷ at 20 °C	$S_0 \rightarrow S_1$ λ_{\max} ϵ (nm) (l mol ⁻¹ cm ⁻¹)	$S_0 \rightarrow S_2$ λ_{\max} ϵ (nm) (l mol ⁻¹ cm ⁻¹)	Third band λ_{\max} ϵ (nm) (l mol ⁻¹ cm ⁻¹)
Methylcyclohexane	2.02	496.5 100	389 19,900 353 21,300	246 17,800
Ethanol	24.58*	491.5 70	356 23,300	245 17,800
Acetonitrile	37.50	484 81	356 20,000	244 14,100

* = at 25 °C

Table 4.5: Solvent effects on the electronic absorption characteristics of N-methyldithiophthalimide

It is noticeable that the absorption coefficients for the $S_0 \rightarrow S_1$ bands of the dithio-compounds are about three times as large as those of the $S_0 \rightarrow S_1$ bands of the monothio-compounds. This may be due partly to a statistical factor, in which a $n \rightarrow \pi^*$ transition becomes twice as likely on account of there being twice the number of sulphur atoms with n electrons, and partly due to the fact that the presence of two sulphur atoms in the same molecule would cause the selection rules governing this transition to be more relaxed.

There is no evidence of a charge-transfer band for N-o-tolylldithiophthalimide: the absorption spectrum is similar to that of N-methyldithiophthalimide. An absorption spectrum of a cis-trans-mixture of N-(4-phenylbut-3-enyl) dithiophthalimide in ethanol solution is also similar to that of N-methyldithiophthalimide.

An investigation of the vibrational fine structure of the ($n \rightarrow \pi^*$) transition of N-methyldithiophthalimide can be made for a methylcyclohexane solution. This is given in Table 4.6.

λ_{max} (nm)	461	494	518	528	552	567	610
Wavenumber (cm^{-1})	21,690	20,240	19,305	18,940	18,115	17,640	16,390
Wavenumber differences (cm^{-1})	1450	935	365	825	475	1250	
		1300		1300			

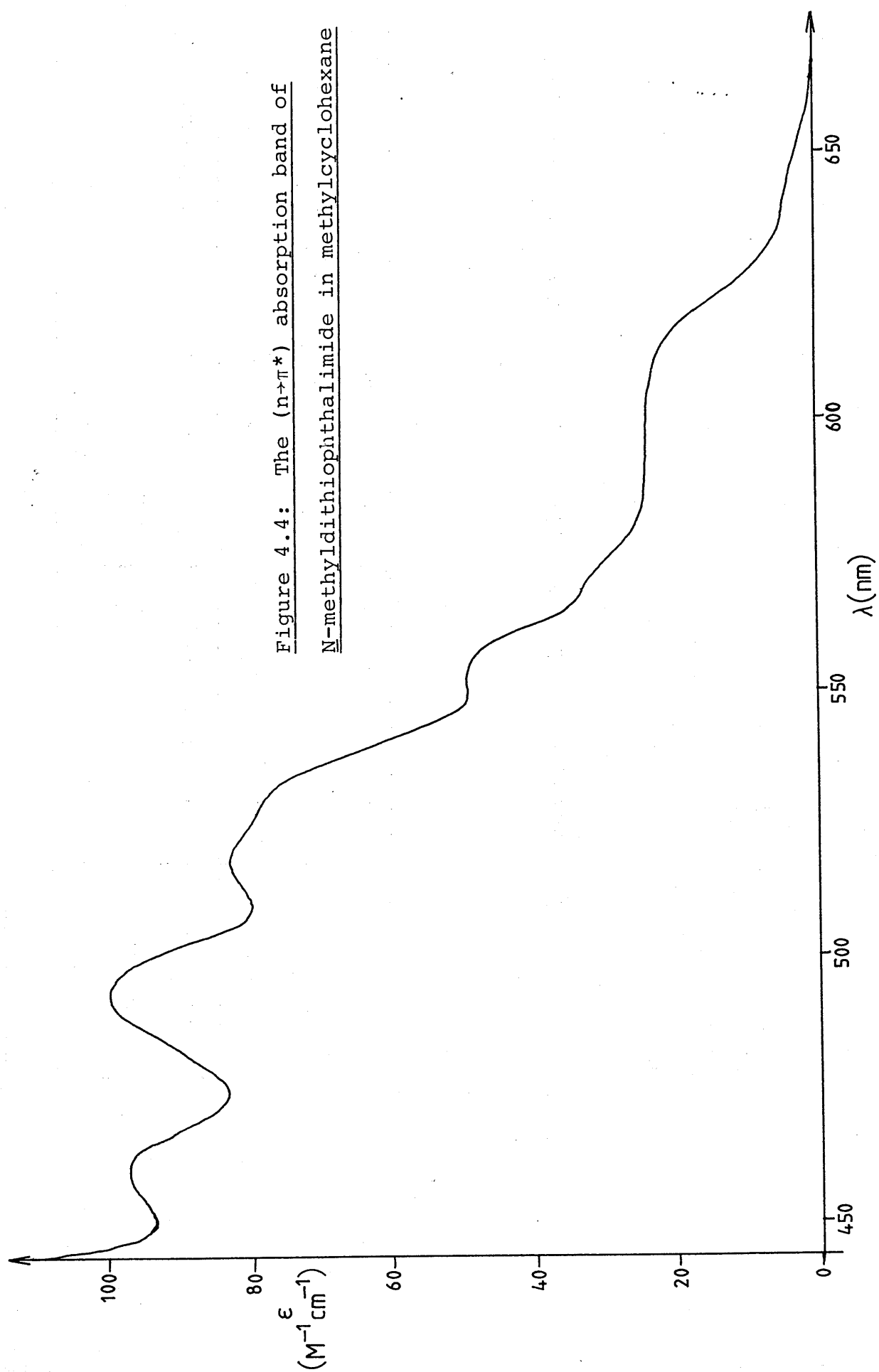
Table 4.6: Vibrational fine structure in the ($n \rightarrow \pi^*$) absorption of N-methyldithiophthalimide

These results do not all fit into a regular vibrational progression, although five of the bands do correspond to a progression with a difference in the range expected for thio-carbonyl compounds. A tetrachloromethane solution infrared

spectrum of N-methyldithiophthalimide shows strong absorptions at $1,329\text{ cm}^{-1}$ and $1,061\text{ cm}^{-1}$, and medium absorptions at $1,216\text{ cm}^{-1}$ and $1,122\text{ cm}^{-1}$.

A long-wavelength tail is observed for N-methyldithiophthalimide, extending to about 670 nm. The absorption coefficient at 650 nm is 4, as shown in Figure 4.4. It is possible that there may be an underlying $S_0 \rightarrow T_1$ absorption, as the small maximum at 650 nm is not part of the vibrational progression (650 nm corresponds to $15,380\text{ cm}^{-1}$, which is $1,005\text{ cm}^{-1}$ from the last entry in Table 4.6).

Figure 4.4: The ($n \rightarrow \pi^*$) absorption band of
N-methyldithiophthalimide in methylcyclohexane



It is interesting to compare the spectrum of N-methyl-dithiophthalimide in ethanol with that of N-methyldithio-succinimide.¹¹⁰ The latter has a ($\pi \rightarrow \pi^*$) band at 322 nm ($\epsilon \sim 4 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) and an ($n \rightarrow \pi^*$) band at 403 nm ($\epsilon = 200 \text{ l mol}^{-1} \text{ cm}^{-1}$), whereas N-methyldithiophthalimide has a $S_0 \rightarrow S_2$ band at 356 nm ($\epsilon = 23,300 \text{ l mol}^{-1} \text{ cm}^{-1}$) and an ($n \rightarrow \pi^*$) band at 491.5 nm ($\epsilon = 70 \text{ l mol}^{-1} \text{ cm}^{-1}$). The longer wavelengths of absorption for N-methyldithiophthalimide are on account of the conjugation of the thiocarbonyl groups with the aromatic ring; the lower absorption coefficients for N-methyldithiophthalimide mean that the transitions are slightly less favourable. These differences are comparable with those observed for N-methylphthalimide and alicyclic imides such as succinimide. Succinimide shows an ($n \rightarrow \pi^*$) transition at around 240 nm ($\epsilon \sim 140 \text{ l mol}^{-1} \text{ cm}^{-1}$) and a ($\pi \rightarrow \pi^*$) transition at about 190-215 nm ($\epsilon \sim 13,000$), whereas N-methylphthalimide⁵ shows a ($\pi \rightarrow \pi^*$) transition with maxima at 292 nm and 300 nm ($\epsilon \sim 1800$ for both maxima) and an ($n \rightarrow \pi^*$) transition which has no clear maximum, but is in the region of 340 nm ($\epsilon \sim 105 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 340 nm).

As the emission characteristics which had been reported for both N-substituted phthalimides and thiocarbonyl compounds were interesting, we carried out some investigations into the emission of the N-methylthiophthalimides.

N-Methyldithiophthalimide shows no emission at room temperature from solution in dichloromethane or ethanol. At liquid nitrogen temperature luminescence with λ_{max} at 657 nm is observed from the dithioimide in an ethanol glass following excitation at 491 nm. This luminescence overlaps with the absorption spectrum. By analogy with aromatic thioketones

and N-methylphthalimide, this luminescence would not be expected to be fluorescence from S_1 . Support for the idea that it is phosphorescence from T_1 arises from the absorption characteristics and the likelihood that the transition around 650 nm in the absorption spectrum is $S_0 \rightarrow T_1$. The emission maximum corresponds to an energy of 182 kJ mol^{-1} ; the S_1 absorption maximum at 491.5 nm corresponds to an energy of 243 kJ mol^{-1} - a singlet-triplet difference of 61 kJ mol^{-1} . For thiobenzophenone the difference between the S_1 absorption maximum^{73(c)}, corresponding to 196 kJ mol^{-1} , and the (n, π^*) triplet energy⁸⁸, corresponding to 159 kJ mol^{-1} , is 37 kJ mol^{-1} . Similar emission behaviour has been found for N-methyldithiosuccinimide¹¹⁰, although it is not remarked upon by the authors.

The position of the second vibrational band of the luminescence is 715 nm; hence the difference between the maxima is $1,240 \text{ cm}^{-1}$, which corresponds to one infrared vibration for the thiocarbonyl group. The quantum yield of luminescence was measured by comparison with zinc tetraphenylporphyrin²⁴⁹, and was found to be approximately 6×10^{-4} . Measurements using the phosphorescence chopper attachment showed the lifetime of the luminescence to be less than 2ms; by comparison, Kanaoka's reported lifetime¹¹⁰ for N-methyldithiosuccinimide in an ethanol glass at 77 K is 2ms. No luminescence was observed following excitation into the third band, and excitation into the $S_0 \rightarrow S_2$ band ($\lambda_{\text{max}} = 356 \text{ nm}$) led to inconclusive results: the position of the lamp overtone (712 nm) makes it difficult to determine whether or not there is any luminescence around 650 - 750 nm. There is no fluorescence from S_2 : this is deduced from the fact that there is no emission band seen at all.

Comparison of the lifetime ($<2\text{ms}$) of the luminescence of N-methyldithiophthalimide with the phosphorescence lifetimes of most of the N-substituted phthalimides⁵, for which the luminescent state is assigned as $^3(\pi, \pi^*)$, show that for the latter the lifetime for the imide in an ethanol glass at 77 K is about 1s. The phosphorescence lifetimes for emission from the $^3(n, \pi^*)$ state of aromatic thioketones⁸¹ are about 3×10^{-5} s. Wirz's work⁹³ on O-alkyl thiobenzoates shows the emitting state of the majority of these compounds to be $T_1(n, \pi^*)$. These are the closest comparison with the N-methylthiophthalimides, in that the O-alkyl thiobenzoates are thioacid derivatives conjugated with an aromatic ring. The phosphorescence lifetimes are <0.5 ms at 77 K and the quantum yields of phosphorescence are ~ 0.2 .

Consequently it is not possible to assign the emitting state of N-methyldithiophthalimide on the basis of lifetime; the possibility of fluorescence from S_1 is also not ruled out on the grounds of lifetime. However, if the general criteria²⁵⁰ for assignment of luminescence are used, it would appear unlikely that the emitting state of N-methyldithiophthalimide is $^3(\pi, \pi^*)$; phosphorescence from such states often has a lifetime exceeding 1s at 77 K, and may show no clear vibrational structure.

The luminescence results observed for N-methyldithiophthalimide show that excitation into the third band gives non-radiative decay, excitation into S_2 gives inconclusive results, and excitation to S_1 leads to a weak luminescence, which may be (n, π^*) phosphorescence. The weakness of the luminescence suggests that much of the decay is non-radiative. It is not possible to determine whether this is due to non-radiative

decay from S_1 or T_1 , or whether the decay is photophysical or photochemical. Certainly the glass is not appreciably decolorised upon carrying out the luminescence experiments. As the glass which was used for the experiment was made from a (room temperature) saturated solution, it is possible that some self-quenching may occur under the experimental conditions, thus lowering the quantum yield.

N-Methylthiophthalimide shows no emission at room temperature in either ethanol or dichloromethane following excitation into the S_1 , S_2 or the third or fourth absorption bands. However, a saturated ethanol or methylcyclohexane glass at 77K shows luminescence following excitation to S_1 , the same luminescence following excitation to S_2 or the third band, and no luminescence following excitation to the fourth band. As with N-methyldithiophthalimide no fluorescence from S_2 was observed: there is no emission which overlaps with the $S_0 \rightarrow S_2$ absorption band. That the same luminescence is observed following excitation into S_2 as follows excitation into S_1 suggests that there is fast internal conversion from S_2 to S_1 .

The positions of the emission maxima and the second vibrational bands of the luminescence are shown in Table 4.7.

Solvent	Emission λ_{\max} (nm)	Second Vibrational band (nm)	Vibrational difference (cm^{-1})
Methylcyclohexane	558	600	1200
Ethanol	553	592	1190

Table 4.7: Luminescence data for N-methylthiophthalimide at 77 K

These vibrational differences are consistent with values expected for a thiocarbonyl vibration. The quantum yield of the luminescence was measured with zinc tetraphenylporphyrin²⁴⁹

as the standard, and found to be about 2×10^{-2} . Lifetime measurements using the phosphorescence chopper apparatus showed the lifetime of the luminescence to be less than 2 ms. The shift to shorter wavelength of the emission maximum on going from a methylcyclohexane glass to an ethanol glass would be consistent with an (n, π^*) emitting state.

As for N-methyldithiophthalimide it would appear most likely that this luminescence is phosphorescence from a $^3(n, \pi^*)$ state, but the possibilities that it is fluorescence from the $(n, \pi^*)S_1$ state may not be ruled out. It would be necessary to carry out some time-resolved work to investigate this luminescence further.

In order to gain some insight into the decay characteristics and possible reaction intermediates of the N-methylthiophthalimides, some quenching experiments were carried out using a nanosecond transient absorption apparatus^{198,251}. The experiments involved the observation of a room-temperature transient by its absorption; the quenching experiments were performed on room temperature solutions of the N-methylthiophthalimides in dichloromethane with nitrogen being bubbled through, using bis(methylthio)ethyne, t-butoxyallene, t-butylthioallene or phenylallene as the quencher. The samples were excited at 308 nm and the decay of the transient absorption at 470 nm (which might be expected to be a triplet-triplet transient absorption by comparison with the results for aromatic thioketones¹⁹⁸) was monitored to give the rate of decay, which was single exponential. The results were plotted as the reciprocal of the lifetime of the transient against the concentration of the quencher. The plots were linear, as in Figure 4.5, and the rate constants which were obtained for

the quenching are given in Table 4.8: these results show quenching in each case at a rate which is close to being diffusion-controlled.

Although these results do not prove conclusively that the photocycloaddition reactions occur from the triplet (n,π^*) state of the thioimides, they provide quite strong evidence in favour of such a mechanism.

Quencher	Rate constant for quenching ($\text{l mol}^{-1} \text{s}^{-1}$)	
	<u>N</u> -methylthiophthalimide	<u>N</u> -methyldithiophthalimide
Phenylallene	1.2×10^9	6.4×10^9
$\text{Bu}^{\text{t}}\text{O}$ allene	4.5×10^9	7.9×10^9
$\text{Bu}^{\text{t}}\text{S}$ allene	3.0×10^{10}	1.1×10^{10}
$\text{MeSC}\equiv\text{CSMe}$	1.3×10^{10}	2.7×10^{10}

Table 4.8: Rate constants for quenching of the transients of the N-methylthiophthalimides with a variety of quenchers.

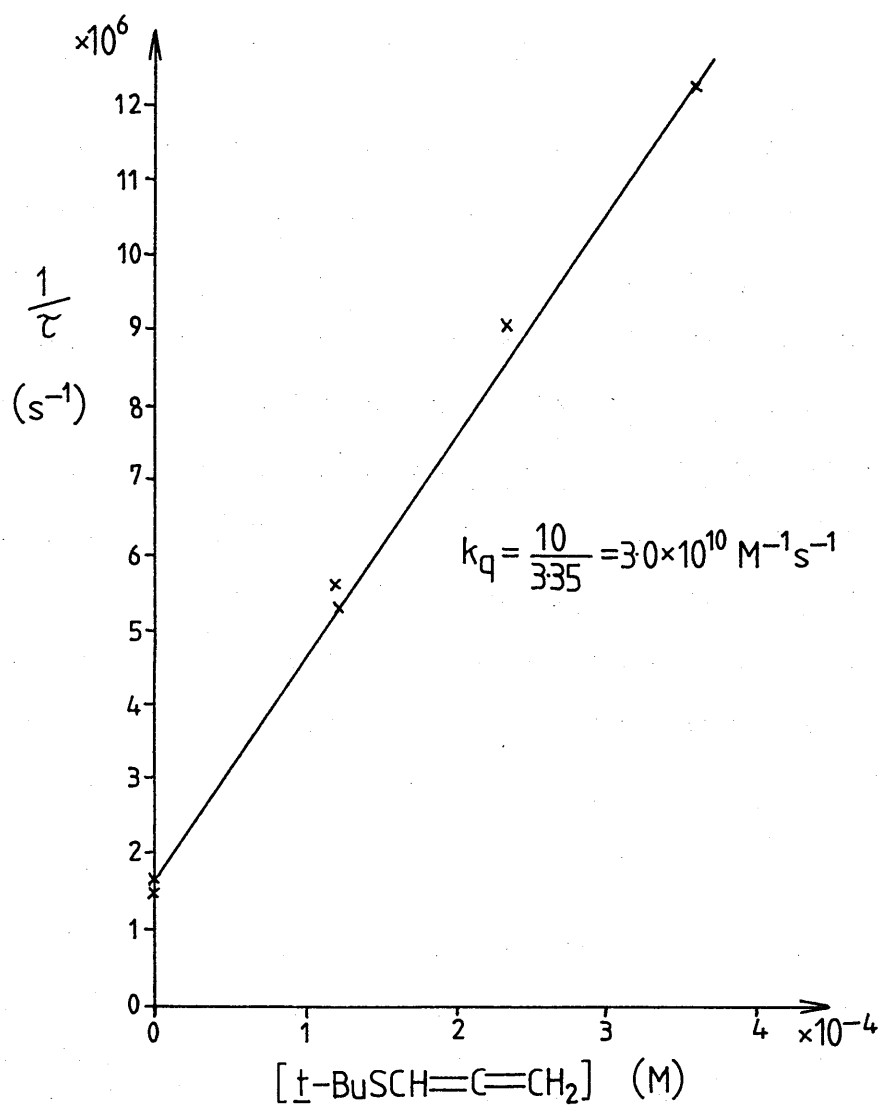


Figure 4.5: Quenching plot for the transient of N-methylthiophthalimide with $t\text{-BuSCH}=\text{C}=\text{CH}_2$

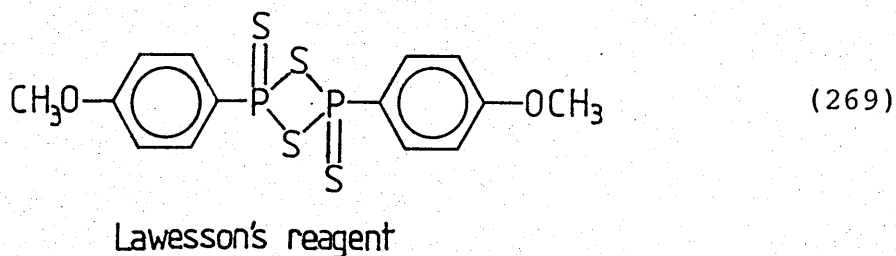
CHAPTER FIVE

GENERAL EXPERIMENTAL PROCEDURES

Preparation of Lawesson's reagent

Lawesson's reagent (269) was prepared according to the literature method,^{221,252} by refluxing phosphorus pentasulphide (20g, 0.090 moles) in anisole (100g, 0.926 moles) for six hours. After cooling the mixture, the resulting crystals were filtered, washed with chloroform and dried. Yield 28g (77%).

Later experiments used commercial Lawesson's reagent (Aldrich, 97%).



Preparation of thiophthalimides by thiation of phthalimides, using Lawesson's reagent

These reactions were carried out according to the literature method.²¹⁹ The phthalimide (0.006 to 0.050 moles) was refluxed with Lawesson's reagent (0.003 to 0.050 moles) in toluene (50 to 250 cm³) for one to four hours. The reaction mixture was then cooled, and the toluene was removed in vacuo. Separation by column chromatography with 1:1 chloroform : toluene as the eluant, gradually increasing the polarity to 100% chloroform for the N-alkylphthalimides, gave crude product fractions, the order of elution being dithiophthalimide, unreacted phthalimide and finally monothiophthalimide.

Ultraviolet irradiation procedures

(i) Small-scale irradiations were carried out using a Hanovia 125-watt medium-pressure mercury arc with a Pyrex water-cooling jacket (cut off²⁴⁷ ~ 275 nm); the outer vessel containing the reaction solution was of approximately 105 cm³ capacity.

(ii) Some of the larger-scale irradiations were carried out using an Applied Photophysics 400-watt medium-pressure mercury arc with a Pyrex water-cooling jacket; the outer vessel containing the reaction solution was of approximately 440 cm³ capacity.

(iii) The other larger-scale irradiations were carried out using a Philips HPL-N 125-watt high-pressure mercury arc without the outer glass bulb, with a Pyrex cooling jacket containing a cupric chloride/calcium chloride/hydrochloric acid filter solution (cut-off \sim 480 nm) which was prepared as described in Calvert and Pitts,²⁵³ using copper(II) chloride dihydrate (200g), calcium chloride (270g), concentrated hydrochloric acid (20 cm³ approx.) in water (1 l). For some reactions the filter solution was used in a more dilute form: this is specified in the detailed experimental text. The outer vessel containing the reaction solution was of approximately 440 cm³ capacity.

Oxygen-free nitrogen was bubbled through the solution for all three types of irradiation. Acetonitrile (HPLC grade, Rathburn Chemicals) was used for some irradiations, and GPR solvents were used for the others.

Physical methods

Infrared spectra were recorded either on a Pye Unicam SP 1050 infrared spectrophotometer or on a Perkin Elmer 1420 ratio-recording infrared spectrophotometer.

Ultraviolet/visible spectra were recorded either on a Pye Unicam SP8-500 ultraviolet/visible spectrophotometer, a Pye Unicam SP8-100 ultraviolet spectrophotometer or a Perkin Elmer 555 ultraviolet/visible spectrophotometer.

Proton nuclear magnetic resonance spectra were recorded on a Perkin Elmer R12B 60 MHz, a Varian EM 360A 60 MHz, a Varian EM 390 90 MHz or a Jeol 90Q 90 MHz Fourier-transform spectrometer. The latter two machines were also used for carbon-13 spectra. Medium-field proton and carbon-13 spectra were obtained on a Perkin Elmer R34 220 MHz continuous-wave spectrometer (courtesy of P.C.M.U., Harwell), a Bruker WP 200 MHz spectrometer or a CFT 20 spectrometer (courtesy of Rijksuniversiteit Utrecht), and high-field spectra were obtained on a Bruker WH 400 MHz spectrometer (courtesy of the University of Warwick). Tetramethylsilane was used as the internal reference for all of the carbon-13 and most of the proton spectra; hexamethyldisiloxane was used for the other proton spectra, and these instances are specified in the detailed experimental text. The chemical shifts for the HMDS spectra are corrected to TMS values by taking the chemical shift of HMDS to be 0.05 ppm. The abbreviations s, d, t and q in the experimental section refer to singlet, doublet, triplet and quartet respectively.

Mass spectra were obtained either on a VG analytical ZAB-IF mass spectrometer (courtesy of P.C.M.U., Harwell) or on a AEI MS 902 or a Kratos MS 80 GCMS (courtesy of Rijksuniversiteit Utrecht).

Microanalytical results were obtained on a Perkin Elmer 240C Elemental Analyzer.

Chromatographic techniques

Thin-layer chromatography (T.L.C.) was carried out using Camlab polygram silica-gel plates with fluorescent indicator. The T.L.C. plates were visualised by long- and short-wave

ultraviolet light, by iodine vapour, or by spraying with a solution of 5% ammonium molybdate in 5% sulphuric acid and then heating to produce a dark blue colour.

Column chromatography was carried out using the flash technique^{254,255} with silica gel, 60H T.L.C. grade (Merck 7736) as the support; any exceptions to this are specified in the experimental chapters.

High-performance liquid chromatography (H.P.L.C.) was carried out on a preparative scale with a Yvon Jobin Miniprep (40 cm column, diameter 2 cm), using silica gel 60, particle size 0.040 - 0.063 mm (Merck 9385) as the support.

CHAPTER SIX

PHOTOCHEMISTRY OF THIOPHTHALIMIDES:

PHOTOCYCLOADDITION REACTIONS

EXPERIMENTAL

Preparations

N-Methylphthalimide

Phthalic anhydride (59.20g, 0.399 moles) was stirred in a flask cooled in an ice-bath whilst methylamine (25% aqueous solution, 60 cm³) was added dropwise; following the addition the reaction mixture was stirred for a further three hours at room temperature before removal of water in vacuo. Toluene was added and was evaporated in vacuo to remove any last traces of water. The crude solid was heated to 160-180 °C for four hours in a round-bottomed flask fitted with an air condenser. After cooling the solid was recrystallised from ethanol to yield white needles (62.06g, 96%).

m.t. 134-135 °C (literature value 134 °C²⁵⁶) IR $\bar{\nu}/\text{cm}^{-1}$: 2930, 1755, 1720, 1655, 1605, 1460, 1380, 1290, 1250, 1185, 1155, 1010, 970, 855, 790, 765, 760, 690. ¹H-NMR (90 MHz, CDCl₃) δ/ppm : 8.00-7.55 (m, 4H), 3.16 (s, 3H). ¹³C-NMR (90 MHz, CDCl₃) δ/ppm : 168.3, 133.8, 132.2, 123.1, 23.8.

N-Methylthiophthalimide from thiophthalimide²¹⁸

Thiophthalimide (4.08g, 0.0250 moles) was dissolved in DMF (25 cm³); diethyl ether (5 cm³), iodomethane (5.33g, 0.0375 moles) and anhydrous potassium carbonate (3.83g, 0.0275 moles) were added to the solution. The suspension was stirred for six hours, and then the flask was covered with aluminium foil and left for two days. The potassium iodide was filtered off and the volatiles were removed in vacuo. The solid product was recrystallised from absolute ethanol, but the melting point of the resulting solid was found to be low (90-91 °C; literature melting point²¹⁸ is 97 °C). A second recrystallisation was carried out using ethyl acetate, but again the melting point of the

resulting solid was found to be low. T.L.C. showed it to be a mixture, and so it was separated by column chromatography, using chloroform, followed by 3% methanol/chloroform as the eluant. $^1\text{H-NMR}$ showed the major fraction to be N-methylthiophthalimide contaminated with N-methylphthalimide, and so it was recrystallised from ethyl acetate to yield pure N-methylthiophthalimide as an orange solid.

m.t. 97-98 °C. IR (nujol mull) $\bar{\nu}/\text{cm}^{-1}$: 1730, 1470, 1375, 1335, 1325, 1175, 1130, 1070, 985, 825, 770, 695. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.05-7.40 (m, 4H), 3.45 (s, 3H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 196.9, 169.3, 136.8, 133.8, 132.9, 127.1, 123.4, 122.4, 27.4.

N-Methylthiophthalimides by thiation of N-methylphthalimide

N-Methylphthalimide (8.08g, 0.0500 moles) and Lawesson's reagent (10.08g, 0.0250 moles) were refluxed in toluene (250 cm^3) for four hours. After cooling the solvent was removed in vacuo and the mixture was separated by column chromatography, using 1:1 chloroform: toluene as the initial eluant and then gradually proceeding to chloroform. The order of elution is N-methyldithiophthalimide, unreacted N-methylphthalimide and finally N-methylthiophthalimide. The N-methylthiophthalimides were recrystallised from ethyl acetate to yield pure orange solid (sometimes needles) N-methylthiophthalimide, 2.83-3.89g (32-44%) and pure purple-brown needles of N-methyldithiophthalimide, 0.87-1.93g (9-20%). The characterisation of N-methylthiophthalimide is as described above.

To obtain N-methyldithiophthalimide as the major product a 1:1 ratio of N-methylphthalimide (0.80g, 0.0050 moles) and

Lawesson's reagent (2.02g, 0.0050 moles) in toluene (50 cm³) was used. Under these conditions the yield of N-methyldithiophthalimide is 0.630g (65%).

N-Methyldithiophthalimide

m.t. 103-104 °C. IR (nujol mull) $\bar{\nu}/\text{cm}^{-1}$: 1465, 1415, 1380, 1365, 1330, 1280, 1200, 1110, 1065, 1005, 965, 915, 770, 765, 750, 650. ¹H-NMR (90 MHz, CDCl₃) δ/ppm : 7.95-7.40 (m, 4H), 3.75 (s, 3H). ¹³C-NMR (90 MHz, CDCl₃) δ/ppm : 197.5, 134.9, 133.0, 123.1, 31.1. Found: C, 55.68; H, 3.43; N, 7.10; S, 33.19; C₉H₇N₂S requires C, 55.96; H, 3.63; N, 7.25; S, 33.16%.

N-(4-Phenylbut-3-enyl)thiophthalimides

N-(3-Bromopropyl)phthalimide (12.00g, 0.0448 moles) and triphenylphosphine (12.00g, 0.0458 moles) were refluxed in xylene (100 cm³) for three hours. The mixture was then allowed to cool overnight, and the solid product was filtered off, washed with xylene, washed with ether, and dried. Yield of phosphonium salt 9.05g (36%).

The phosphonium salt (9.00g, 0.017 moles) was dissolved as far as possible in water (75 cm³). Dichloromethane (50 cm³) was added and the mixture was stirred vigorously. Sodium hydroxide solution (20 cm³ of 1M solution) was added dropwise over five minutes. The mixture was stirred for a further ten minutes, and then as the aqueous layer was found to be only very slightly alkaline further sodium hydroxide solution (20 cm³) was added, and the reaction mixture was stirred for a further fifteen minutes, before being placed in a separating funnel in order to separate the layers. The aqueous layer was extracted three times with dichloromethane, the extracts were combined and left to stand overnight over

anhydrous magnesium sulphate. The aqueous layer was also left to stand overnight.

The following day, two crops of white solid were obtained from the aqueous layer; these were filtered, washed and dried. The dichloromethane solution was filtered off from the magnesium sulphate and was evaporated in vacuo to yield a white solid. This was recrystallised from chloroform/40-60 petrol ether to yield two crops of white solid. As it appeared that some product crystals were present with the magnesium sulphate, this was heated in absolute ethanol and the solution was filtered while hot. After cooling, the ethanol was removed in vacuo and the residue was recrystallised from chloroform/40-60 petrol ether to yield a further crop of white solid. All of the white solid samples showed the same IR spectrum, and all were the phosphorane, yield 5.86g (77%).

The phosphorane proved to be fairly insoluble in cold dichloromethane, industrial methylated spirit or dimethylformamide. Eventually the final stage of the Wittig reaction was carried out by refluxing the phosphorane (5.50g, 0.0122 moles) with benzaldehyde (3.87g, 0.0365 moles had been added by this stage) in dimethylformamide (40 cm³) for two hours. The reaction mixture was cooled, and then the solvent and unreacted benzaldehyde were removed in vacuo to yield a brown oil. A ¹H-NMR spectrum of the brown oil showed it to contain triphenylphosphine oxide as well as alkene products, and so it was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant, gradually proceeding to 25% methanol/chloroform. Four fractions were obtained, of which the first consisted of the alkene products cis- and trans-N-

(4-phenylbut-3-enyl) phthalimide in the approximate ratio 83% trans and 17% cis. Yield 2.37g (70%).

In order to carry out the thiation reaction, N-(4-phenylbut-3-enyl)phthalimide (1.70g, 0.0061 moles) and Lawesson's reagent (1.24g, 0.0031 moles) were refluxed in toluene (25 cm³) for two hours. After cooling, the solvent was removed in vacuo and the reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant, and gradually proceeding to chloroform. The crude dithio- and monothio- products were obtained as brown and orange oils, (0.47g, 25% and 1.31g, 73%) respectively: both contained mixtures of the cis- and trans- isomers. A sample of the monothio-product was purified further by column chromatography, with 1:1 chloroform:toluene as the eluant, before microanalysis, but not before irradiation. The dithio-product was purified by column chromatography with 1:1 chloroform:toluene as eluant before characterisation and irradiation.

Triphenyl(3-phthalimidopropyl)phosphonium bromide

m.t. 212-213 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 3450, 3020, 2800, 1767, 1715, 1585, 1465, 1440, 1405, 1377, 1185, 1115, 1085, 1005, 995, 805, 755, 750, 730, 720, 685. ¹H-NMR (90 MHz, D₂O) δ/ppm : 7.90-7.50 (m, 22H), 3.85-3.60 (m, 2H), 3.60-2.90 (m, 2H) 2.30-1.80 (m, 2H). ¹³C-NMR (90 MHz, D₂O) δ/ppm : 247.9, 208.7, 182.9, 173.0, 137.7, 136.4, 135.9, 133.6, 133.0, 132.5, 129.5, 126.2, 122.3, 118.4, 79.7, 71.3, 57.0, 54.8, 42.6, 41.0, 40.2, 39.5, 38.0, 23.1, 22.5, 21.8, 17.7, 16.6. Found: C, 65.54; H, 4.54; N, 2.61; C₂₉H₂₅; NO₂PBr requires C, 65.66; H, 4.72; N, 2.64%.

Triphenyl(3-phthalimidopropylidene)phosphorane

m.t. 214-215 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 3400, 3060, 2930, 1640, 1585, 1565, 1440, 1370, 1315, 1115, 995, 825, 745, 725, 690. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.00-7.20 (m, 22H), 3.60 (m, 4H), 2.33 (s, 3H), 1.90 (m, 2½H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 176.3, 169.6, 142.9, 135.0, 133.9, 133.4, 130.9, 130.3, 129.0, 127.5, 126.6, 120.1, 116.2, 39.5, 38.7, 22.6, 21.1, 18.8.

Cis-and trans-N-(4-phenylbut-3-enyl)phthalimide

m.t. 53-60 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 2930, 1775, 1715, 1700, 1465, 1450, 1400, 1365, 1340, 1110, 990, 875, 790, 720, 695. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 7.90-7.40 (m, 4H), 7.30-7.00 (m, 5H), 6.50 (dt, $J = 12\text{Hz}, 1\text{Hz}, 0.78\text{H}$), 6.40 (d, $J = 8\text{Hz}$) and 6.20 (t, $J = 8\text{Hz}$) (together 0.33H), 5.64 (dt, $J = 12\text{Hz}, 7.5\text{Hz}, 0.78\text{H}$), 3.78 (two close t's, $J = 7.5\text{Hz}, 2\text{H}$), 2.72 (two close dt's $J = 7.5\text{Hz}, 7.5\text{Hz}, 2\text{H}$). This shows 1.56:0.33 trans:cis = 83% trans:17% cis. $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 168.1, 136.8, 134.3, 133.8, 132.4, 131.9, 131.6, 129.6, 128.9, 128.5, 128.4, 128.1, 127.7, 127.1, 126.7, 126.0, 123.0, 37.5, 32.2, 27.7. Found: C, 77.32; H, 5.17; N, 4.85; $\text{C}_{18}\text{H}_{15}\text{NO}_2$ requires C, 77.98; H, 5.42; N, 5.05%.

Cis-and trans-N-(4-phenylbut-3-enyl)thiophthalimide

IR (oil smear) $\bar{\nu}/\text{cm}^{-1}$: 1745, 1715, 1595, 1470, 1385, 1355, 1345, 1300, 1265, 1155, 1120, 930, 770, 700. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.40-6.80 (m, 9H), 6.47 (dt, $J = 12\text{Hz}, 1\text{Hz}, 0.55\text{H}$), 6.31 (s, 0.17H), 6.20 (t, $J = 7.5\text{Hz}, 0.17\text{H}$), 5.65 (dt, $J = 12\text{Hz}, 7.5\text{Hz}, 0.72\text{H}$), 4.10 (two t's, $J = 7.5\text{Hz}, 2\text{H}$), 3.75 (d, $J = 2\text{Hz}, 1.33\text{H}$), impurity, 2.73 (dt, $J = 7.5\text{Hz}, 7.5\text{Hz}, 2\text{H}$); shows 1.27:0.34 trans:cis = 79%: 21% trans:cis. $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 196.1, 169.0, 163.7, 136.7, 136.5, 134.4, 133.5, 132.7, 131.9, 131.2, 128.2, 128.0, 127.8, 127.2, 126.8, 126.6, 126.4, 125.7, 123.3, 122.6, 122.2, 114.1, 113.8, 113.3, 55.1, 40.0,

31.3, 27.0. The small absorptions at 169.0 and 27.0 may be caused by the presence of some cis and trans N-(4-phenylbut-3-enyl)thiophthalimide.

Cis-and trans-N-(4-phenylbut-3-enyl)dithiophthalimide

IR (oil smear) $\bar{\nu}/\text{cm}^{-1}$: 1470, 1355, 1320, 1295, 1280, 1150, 1075, 1055, 770, 700. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 7.75-7.30 (m, 4H), 7.30-7.00 (m, 5H), 6.45 (dt, $J = 13\text{Hz}$, 1Hz, 0.75H), 6.30 (s, 0.5H), 6.20 (t, $J = 7.5\text{Hz}$, 0.25H), 5.65 (dt, $J = 13\text{Hz}$, 7.5Hz, 0.5H), 4.47 (two t's, $J = 9\text{Hz}$, 2H), 2.60 (m, 2H); shows 1.25: 0.75 trans:cis = 63% trans: 37% cis. $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 196.7, 134.5, 132.8, 132.1, 131.5, 128.5, 128.3, 128.0, 127.5, 127.1, 126.7, 126.0, 125.8, 123.0, 43.2, 43.0, 31.5, 27.2.
Found: C, 69.86; H, 5.03; N, 4.41; S 20.70; $\text{C}_{18}\text{H}_{15}\text{NS}_2$ requires C, 69.90; H, 4.85; N 4.53; S, 20.71%.

Irradiations

Control irradiation of thiophthalimide

Thiophthalimide (1.00g, 0.0061 moles) was dissolved as far as possible in acetonitrile (105 cm^3) and irradiated according to method(i). The reaction was monitored by T.L.C. using both 5% methanol/chloroform and 1:1 chloroform:toluene as eluants, and was stopped after forty-eight hours when T.L.C. showed that little reaction had occurred. The solvent was removed in vacuo, and IR and $^1\text{H-NMR}$ spectra showed only unchanged starting material to be present.

Control irradiation of N-methylthiophthalimide

N-Methylthiophthalimide (24mg, 1.4×10^{-4} moles) was dissolved in acetonitrile (12 cm^3) and irradiated for fifty-seven hours in a Pyrex test-tube which was attached to the Pyrex probe of a 400W medium-pressure mercury arc by an elastic band. The

reaction was followed by T.L.C. using 5% methanol/chloroform as the eluant, and it was seen that the sole product was N-methylphthalimide.

Control irradiation of N-methyldithiophthalimide

N-Methyldithiophthalimide (1.00g, 0.0052 moles) was dissolved in acetonitrile (105 cm³) and irradiated according to method(i). The reaction was monitored by T.L.C. using 1:1 chloroform:toluene as the eluant. The reaction was stopped after fifty hours and the solvent was removed in vacuo. The ¹H-NMR spectrum of the reaction mixture was as follows (60MHz, CDCl₃) δ/ppm: 7.95-7.10 (m, 4H), 3.75 (s, 2 $\frac{1}{4}$ H), 3.40 (s, $\frac{1}{3}$ H), 3.15 (s, $\frac{1}{6}$ H), 2.35 (m, $\frac{1}{6}$ H), 2.00 (m, $\frac{1}{6}$ H). (If all of the components present in the mixture are assumed to show N-CH₃ between 3.00 and 4.00 ppm, then the integration of the N-CH₃ absorptions suggests that about 75% of the mixture is unreacted starting material, for which the N-CH₃ absorption is 3.75 ppm.)

The mixture was recrystallised from ethyl acetate in order to remove some (0.37g) of the unchanged starting material, and the solvent was removed from the mother liquor in vacuo. The residue was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to 3:1 chloroform:toluene, to yield eight fractions, of which the first two were unreacted starting material, the following four were oxidation products (the IR spectra show strong C=O absorptions at 1740 or 1725 cm⁻¹), and the last two (11 and 10% by weight) were high-molecular-weight products (the lowest R_f product being dark green). The structure of these products could not be determined.

N-Methylthiophthalimide with *trans*-stilbene

N-Methylthiophthalimide (0.89g, 0.0050 moles) and *trans*-stilbene (1.35g, 0.0075 moles) were dissolved in benzene (105 cm³) and irradiated according to method(i). The reaction was monitored by T.L.C. using 5% methanol/ chloroform as eluant, and was stopped after six hours. The products were separated by column chromatography using 1:1 chloroform: toluene as the initial eluant and gradually increasing the polarity to chloroform. Eight fractions were obtained of which the first was unreacted stilbene (0.78g), the second unreacted N-methylthiophthalimide (0.14g), and the third N-methylphthalimide (0.01g, 15% based on reacted N-methylthiophthalimide). The fourth and seventh were low-yield minor products. The fifth and eighth were recrystallised from absolute ethanol to give materials that were shown by MS and IR spectra to be identical; this white solid was obtained in yields of 25% crude, 6% pure. The sixth fraction was the major product; this was also recrystallised from absolute ethanol to give 2-methyl-3', 4'-diphenyl 2,3-dihydro-1H-isoindole-3-spiro-2'-thietan-1-one as a white solid, yield 45% crude, 17% pure.

2-Methyl-3',4'-diphenyl-2,3-dihydro-1H-isoindole-3-spiro-2'-thietan-1-one (major *trans*-isomer).

m.t. 193-196 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1708, 1612, 1598, 1495, 1470, 1410, 1375, 1135, 1060, 750, 735, 710, 685, 675. ¹H-NMR (90 MHz, CDCl₃) δ/ppm : 8.20-6.50 (m, 14H), 5.53 (d, J = 10Hz, 1H), 5.42 (d, J = 10Hz, 1H), 3.04 (s, 3H). ¹³C-NMR (90 MHz, CDCl₃) δ/ppm : 167.5, 147.8, 140.6, 136.8, 132.5, 131.7, 130.9, 129.4, 128.9, 128.7, 128.3, 127.7,

127.5, 125.9, 125.8, 125.1, 124.4, 123.3, 73.0, 62.0, 42.7, 26.1. Found: C, 77.46; H, 5.38; N, 3.90; S, 8.93; $C_{23}H_{19}NOS$ requires C, 77.28; H, 5.32; N, 3.92; S, 8.97%. MS m/z 235 ($M-C_7H_6S$ (= thiobenzaldehyde), 235.100; $C_{16}H_{13}NO$ requires 235.100), 180 (base), 165, 121.

Minor trans-isomer

m.t. 236-238 °C. IR (1% KBr disc) $\bar{\nu}/cm^{-1}$: 1715, 1470, 1455, 1430, 1390, 1130, 1070, 935, 800, 780, 765, 745, 695, 680. 1H -NMR (90 MHz, d_3 - CH_3CN) δ/ppm : 7.95-7.75 (m, 1H), 7.75-7.25 (m, 9H), 7.25-6.80 (m, 5H), 5.68 (d, $J = 16$ Hz, 1H), 4.97 (d, $J = 16$ Hz, 1H), 3.35 (s, 3H). ^{13}C -NMR (90 MHz, d_6 -acetone) δ/ppm : (impure) 166.2, 141.8, 131.9, 131.8, 130.2, 130.1, 129.5, 128.5, 128.0, 127.7, 127.4, 134.1, 122.2, 108.2, 71.8, 45.0, 24.4; (90 MHz, $CDCl_3$): includes 30.5. Found: C, 77.16; H, 5.28; N, 4.07; $C_{23}H_{19}NOS$ requires C, 77.28; H, 5.32; N, 3.92%. MS m/z 325 ($M-S$, 325.147; $C_{23}H_{19}NO$ requires 325.147), 248, 234, 180, 178, 146, 117, 91, 77, 31(base).

The reaction was carried out again using N-methylthiophthalimide (1.00g, 0.0056 moles) and trans-stilbene (1.50g, 0.0083 moles), and irradiating according to method (i) for thirty hours. Column chromatography gave unreacted stilbene (0.71g) unreacted N-methylthiophthalimide (0.33g), N-methylphthalimide (15mg, 2%), major product isomer (1.00g, 74% crude; 0.42g, 31% pure), and a fraction containing a mixture of minor products. This latter was separated on a silica column, using chloroform as the initial eluant and gradually proceeding to 8% methanol/chloroform. This gave four fractions of which the first was major product isomer (0.22g, 16% crude; 90mg, 7% pure), the second was minor product isomer (100mg, 7% crude; 51mg, 4% pure), and the third and fourth (123mg total) were other minor products, shown by 1H -NMR to be

mixtures. These were recrystallised but the solids obtained (20mg) were also seen to be mixtures ($^1\text{H-NMR}$).

N-Methyldithiophthalimide with *trans*-stilbene

N-Methyldithiophthalimide (1.00g, 0.0052 moles) and *trans*-stilbene (1.87g, 0.0104 moles) were dissolved in benzene (105 cm³) and irradiated according to method(i). The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as the eluant, and was stopped after eight hours. The solvent was removed in vacuo and the reaction mixture was separated by column chromatography using 1:1 chloroform:toluene as the initial eluant and then gradually increasing the polarity to chloroform. Eight fractions were obtained, of which the first three consisted of unreacted starting materials (0.78g approx. N-methyldithiophthalimide and 1.27g approx. *trans*-stilbene, calculated from the masses of the fractions and the ratio of the integration of the N-Me singlet of N-methyldithiophthalimide to the integration of the aromatic absorptions in the $^1\text{H-NMR}$ spectra). The fourth and fifth fractions were recrystallised from absolute ethanol to give the major product, yield 437mg, 100% crude; 195mg, 46% pure. The small (35mg) sixth fraction consisted of a minor product, which was recrystallised from absolute ethanol, yield 2mg pure. The seventh and eighth fractions showed the presence of oxidation products (IR shows C=O absorptions at 1740 cm⁻¹ and 1715 cm⁻¹ respectively); in addition neither gave clear $^1\text{H-NMR}$ spectra.

2-Methyl-3',4'-diphenyl-2,3-dihydro-1H-isoindole-3-spiro-2'-thietane-1-thione

m.t. 145-147 °C. IR (1% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1500, 1475, 1455, 1380, 1345, 1320, 1130, 1040, 765, 740, 720, 695, 675.

$^1\text{H-NMR}$ (90MHz, CDCl_3) δ /ppm: 8.30-6.50 (m, 14H), 5.60 (d, $J = 11\text{Hz}$, 1H), 5.48 (d, $J = 11\text{Hz}$, 1H), 3.41 (s, 3H). $^{13}\text{C-NMR}$ (90MHz, CDCl_3) δ /ppm: 193.2, 145.7, 140.3, 137.0, 136.6, 132.4, 129.9, 129.1, 128.9, 128.6, 127.8, 125.6, 125.2, 124.8, 122.8, (78.4 in d_6 -benzene), 61.9, 42.9, 31.9. Found: C, 73.52; H, 5.12; N, 3.63; S, 17.43; $\text{C}_{23}\text{H}_{19}\text{NS}_2$ requires C, 73.96; H, 5.13; N, 3.75; S, 17.15%. MS m/z 341 (M-S, 341.123; $\text{C}_{23}\text{H}_{19}\text{NS}$ requires 341.124), 250, 180 (base), 165, 146, 121, 76.

Minor product

m.t. 184-186 $^{\circ}\text{C}$. IR (1% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1475, 1455, 1425, 1365, 1340, 1320, 1125, 1095, 940, 765, 740, 715, 690.

N-Methylthiophthalimides with trans-stilbene and white light

Six Pyrex test-tubes were set up next to a 60W tungsten bulb; the contents were as follows:

	<u>N-methylthiophthalimide</u>	<u>trans-stilbene</u>	<u>solvent (12 cm³)</u>
(i)	71mg, 4.0×10^{-4} moles	107mg, 6.0×10^{-4} moles	benzene
(ii)	" " " "	" " " "	dichloromethane
(iii)	" " " "	" " " "	dichloromethane + 4 drops pyridine
	<u>N-methyldithiophthalimide</u>	<u>trans-stilbene</u>	<u>solvent (12 cm³)</u>
(iv)	71mg, 3.7×10^{-4} moles	99mg, 5.5×10^{-4} moles	benzene
(v)	" " " "	" " " "	dichloromethane
(vi)	" " " "	" " " "	dichloromethane + 4 drops pyridine

The reactions were monitored by T.L.C. using 1:1 chloroform: toluene as the eluant. In the case of N-methylthiophthalimide more minor products were apparent on T.L.C. in the benzene sample than in the dichloromethane samples, although $^1\text{H-NMR}$ spectra of the three reaction mixtures did not appear to differ greatly. A white solid was also formed in the benzene sample: this was filtered, dried, and shown by IR to be of

the same composition as the minor product which was formed in the N-methylthiophthalimide/trans-stilbene medium-pressure mercury arc experiment.

For N-methyldithiophthalimide T.L.C. showed that the same products were formed in all cases, but that the distribution of the minor products was different for the benzene and the dichloromethane solutions. This was confirmed by $^1\text{H-NMR}$.

Thiophthalimide with trans-stilbene

Thiophthalimide (0.82g, 0.0050 moles) and trans-stilbene (1.35g, 0.0075 moles) were dissolved as far as possible in benzene (105 cm³) and irradiated according to method(i). The solution was stirred periodically in order to dissolve any previously undissolved thiophthalimide. The reaction was monitored by T.L.C. using 1:1 chloroform:toluene as eluant, and was stopped after sixteen-and-a-half hours. The solvent was removed in vacuo and the reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant, and gradually increasing the polarity to 10% methanol/chloroform. Nine fractions were obtained, of which the first was unreacted stilbene (0.79g crude), and the second was impure unreacted thiophthalimide. The remaining seven were all shown by $^1\text{H-NMR}$ to be mixtures. The third and fourth fractions showed some interesting $^1\text{H-NMR}$ features (5.50 (d, $J = 11\text{Hz}$), 4.35 (d, $J = 11\text{Hz}$) and 5.40 (d, $J = 11\text{Hz}$), 4.30 (d, $J = 11\text{Hz}$), respectively); however $^{13}\text{C-NMR}$ of the third and eighth fractions showed them to be mixtures including large numbers of aliphatic absorptions. Attempts to recrystallise fractions three, four and seven,

which had appeared relatively pure by T.L.C. and ^1H -NMR, from absolute alcohol led only to the formation of brown solids; further attempts at recrystallisation using toluene gave only small quantities of impure solids.

N-Methylthiophthalimide with *cis*-stilbene

N-Methylthiophthalimide (1.00g, 0.0056 moles) and *cis*-stilbene (1.50g, 0.0085 moles) were dissolved in benzene (440 cm³) and irradiated according to method (iii), with the cut-off of the filter solution ~ 480 nm. The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as the eluant, and was stopped after thirty-one-and-a-half hours. The solvent was removed in vacuo and the reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to 8% methanol/chloroform. Seven fractions were obtained of which the first was a mixture of *cis*- and *trans*-stilbene (1.05g, containing approximately 60% *cis*- and 40% *trans*-stilbene, as calculated from the relative integrations of the PhCH absorptions in the ^1H -NMR spectrum), the second was unreacted N-methylthiophthalimide (0.34g), and the third was a mixture of unreacted N-methylthiophthalimide and N-methylphthalimide (yield of N-methylphthalimide calculated from the relative integrations of the NMe absorptions in the ^1H -NMR to be 10mg, 2%). The fourth fraction was recrystallised from absolute ethanol to yield the *trans*-product major isomer (the same major product as from the reaction of N-methylthiophthalimide with *trans*-stilbene), yield 0.45g (34%). The structure of this product was confirmed by comparison of the IR and ^1H -NMR spectra with those of the major product from the *trans*-stilbene experiment.

The fifth fraction was dissolved as far as possible in hot absolute ethanol; the insoluble material was filtered off, washed with absolute ethanol and dried. This was shown by IR and melting temperature to be identical to the trans-product minor isomer from the reaction of N-methylthiophthalimide with trans-stilbene. Yield 18mg (1%). The soluble material was precipitated out as a white solid by the addition of water: this was found to be a mixture of minor products. The sixth fraction was found to be a mixture of minor products; this could not be recrystallised from absolute ethanol, even after the addition of water, and was characterised in an impure state.

Sixth fraction

IR(1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 3452, 1703, 1470, 1453, 1420, 1378, 1352, 1035, 758, 731, 710, 697. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 9.70-9.15 (m, 1H), 8.50-6.50 (m, 17H), 5.95-5.30 (m, 1H), 5.30-4.60 (m, 1H), 4.55-4.20 (m, 1H), 3.45 (s, $\frac{1}{2}\text{H}$), 3.05 (s, $\frac{1}{3}\text{H}$), 2.85 (s, $\frac{1}{2}\text{H}$), 2.16(s) and 2.13(s), together 1H, 2.06 (s, 1H), 1.97 (s, 1H), 1.75 (s, $\frac{2}{3}\text{H}$), 1.25 (m, $\frac{1}{2}\text{H}$, impurity). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 170, 169, 168, 167, 147.2, 143.4, 136.5-122.6 (29 absorptions), 74.1, 73.9, 56.6, 55.9, 54.6, 52.4, 52.3, 51.9, 51.6, 47.2, 46.6, 45.6, 35.7, 35.4, 33.3, 29.0, 28.8, 28.5, 27.9, 24.9.

N-Methylthiophthalimide with 1,1-diphenylethene

N-Methylthiophthalimide (1.00g, 0.0056 moles) and 1,1-diphenylethene (1.50g, 0.0083 moles) were dissolved in acetonitrile (250 cm^3) and irradiated according to method(ii). The reaction was monitored by T.L.C. using 1:1 chloroform: toluene as eluant, and was stopped after eight-and-a-half hours.

The solvent was removed in vacuo, and the reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and then increasing the polarity to chloroform. The fractions were 1,1-diphenylethene (0.87g crude), unreacted N-methylthiophthalimide (0.51g crude), N-methylphthalimide (3mg, <1% yield), major product and minor product. The major product was recrystallised three times from absolute ethanol to give white crystals, yield 0.299g (35%). The minor product decomposed during attempts to recrystallise it from absolute ethanol, and the IR, ^1H - and ^{13}C -NMR spectra taken previously were insufficient for characterisation.

3-(Diphenylmethylene)-2-methyl-2,3-dihydro-1H-isoindol-1-one
m.t. 173-178 °C. IR (1% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1700, 1620, 1475, 1425, 1370, 1340, 1035, 1025, 765, 705. ^1H -NMR (90 MHz, CDCl_3) δ/ppm : 7.85 (m, 1H), 7.70-7.00 (m, 12H), 6.40 (m, 1H), 2.89 (s, 3H). ^{13}C -NMR (90 MHz, CDCl_3) δ/ppm : 169.1, 141.3, 140.9, 137.5, 135.2, 131.3, 130.9, 130.7, 130.3, 129.9, 129.8, 129.5, 128.9, 128.3, 128.1, 127.8, 127.3, 127.0, 126.0, 123.3, 122.8, 122.5, 31.5.
Found: C, 84.91; H, 5.43; N, 4.27; $\text{C}_{22}\text{H}_{17}\text{NO}$ requires C, 84.88; H, 5.47; N, 4.50%. MS m/z 311, (M^+ , base, 311.131; $\text{C}_{22}\text{H}_{17}\text{NO}$ requires 311.130), 252, 234, 156, 91.

N-Methyldithiophthalimide with 1,1-diphenylethene/medium-pressure mercury arc

N-Methyldithiophthalimide (1.00g, 0.0052 moles) and 1,1-diphenylethene (1.50g, 0.0083 moles) were dissolved in acetonitrile (105 cm^3) and irradiated according to method(i). The reaction was monitored by T.L.C. using 1:1 chloroform:toluene as the eluant, and was stopped after thirty-six hours.

The solvent was removed in vacuo and the mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to chloroform. The first fraction, which was the largest, consisted of unreacted starting materials (both IR and ^1H -NMR spectra showed a mixture of N-methyldithiophthalimide with 1,1-diphenylethene); the following two contained products, but further purification by recrystallisations using 95% ethanol and ethyl acetate/60-80 petroleum ether gave purer samples of the products which were shown by IR to be oxidation products (i.e. to contain C=O groups). The remaining fractions were small and impure.

N-Methyldithiophthalimide with 1,1-diphenylethene/high-pressure mercury arc

N-Methyldithiophthalimide (1.00g, 0.0052 moles) and 1,1-diphenylethene (1.40g, 0.0078 moles) were dissolved in benzene (440 cm³) and irradiated according to method (iii); the cut-off of the filter solution was about 475 nm. The reaction was monitored by T.L.C. using 1:1 chloroform:toluene as the eluant, and was run for fifty-five hours. Both IR and ^1H -NMR spectra of the reaction mixture indicated that the main components were unreacted starting materials; the reaction mixture was then irradiated further under the same conditions, such that the total reaction time was one hundred hours. ^1H -NMR and IR spectra showed that the main components of the mixture were oxidised and unreacted starting materials. However the lowest R_f fraction which was eluted contained a dark-green, rather insoluble product which appeared similar to that from the control irradiation of N-methyldithiophthalimide.

N-Methylthiophthalimide with 2,3-dimethylbut-2-ene

N-Methylthiophthalimide (1.00g, 0.0056 moles) was dissolved as far as possible in 2,3-dimethylbut-2-ene (12.00g, 0.143 moles). The mixture was divided between two Pyrex tubes, which were attached to the Pyrex filter of a 400W medium-pressure mercury arc. The reaction was monitored by T.L.C., using 5% methanol/chloroform as the eluant, and was stopped after four-and-a-half hours. The volatiles were removed in vacuo, and the product mixture was separated by column chromatography. Nine fractions were obtained. The first was a mixture of unreacted N-methylthiophthalimide with a product as seen by ^1H -NMR and IR; this fraction was separated further by column chromatography, using chloroform as the eluant, and recrystallisation from ethyl acetate was attempted for those fractions containing the most product, but this could not be purified. The second fraction was unreacted N-methylthiophthalimide (0.47g). The third was N-methylphthalimide (crude yield 74mg, 15%). The fourth fraction was a viscous yellow oil, which appeared by ^1H -NMR to be impure; it was separated on a further column using chloroform as the eluant to give three fractions, of which the second was pure major product, a yellow oil which could not be recrystallised (yield 50mg, 6%). The fourth, fifth, sixth, seventh and ninth fractions from the original column were small and impure, but the eighth was shown by comparison of ^1H -NMR, ^{13}C -NMR and IR spectra with those of an authentic sample to be pinacol (70mg).

2,3',3',4',4'-Pentamethyl-2,3-dihydro-1H-isoindole-3-spiro-2'-thietan-1-one

IR (oil smear) $\bar{\nu}/\text{cm}^{-1}$: 2980, 1705, 1610, 1470, 1415, 1355, 1235, 1145, 1120, 1035, 950, 815, 795, 750, 725, 690, 680. $^1\text{H-NMR}$ (220 MHz, CDCl_3) δ/ppm : 8.00 (d, $J = 9\text{Hz}$, 1H), 7.82 (d, $J = 9\text{Hz}$, 1H), 7.65 (t, $J = 9\text{Hz}$, 1H), 7.50 (t, $J = 9\text{Hz}$, 1H), 3.50 (s, 3H), 1.70 (s, 3H), 1.69 (s, 3H), 1.22 (s, 3H), 1.01 (s, 3H). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ/ppm : 168.8, 147.5, 130.7, 128.6, 128.4, 125.8, 122.7, 93.9, 56.7, 46.9, 30.0, 29.4, 29.1, 26.4, 23.5. MS m/z 214 ($\text{M-CH}_3\text{S}$), 187 ($\text{M-(CH}_3)_2\text{C=S}$ (187.099; $\text{C}_{12}\text{H}_{13}\text{NO}$ requires 187.100)), 178, 172, 117, 84 (base), 69, 41.

N-Methylthiophthalimide with 2,3-dimethylbut-2-ene in acetonitrile

N-Methylthiophthalimide (1.00g, 0.0056 moles) and 2,3-dimethylbut-2-ene (0.95g, 0.0113 moles) were dissolved in acetonitrile (440 cm^3) and irradiated according to method (ii). The reaction was followed by T.L.C., using 1:1 chloroform:toluene as eluant, and was stopped after two hours. The solvent was removed in vacuo and a $^1\text{H-NMR}$ spectrum was taken of the reaction mixture: this showed that a larger number of products had been formed than in the previous reaction. The mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to 2% methanol/chloroform. Seven fractions were obtained, of which the first was unreacted N-methylthiophthalimide together with a product, the second and third were small and impure, as seen by T.L.C. and $^1\text{H-NMR}$, the fourth was N-methylphthalimide, the fifth and sixth were small and impure, as seen by $^1\text{H-NMR}$ and T.L.C., and the seventh was large but impure. This seventh fraction was

separated further by column chromatography, using 1:1 chloroform:toluene as the initial eluant, and proceeding to chloroform. Six fractions were obtained of which the first was N-methylphthalimide and the remaining five were mixtures of products. ¹H-NMR showed the major product from the first experiment to be present in three of these fractions. No further separation was carried out.

N-Methylthiophthalimide with methylenecyclohexane

N-Methylthiophthalimide (1.00g, 0.0056 moles) and methylenecyclohexane (0.81g, 0.0084 moles) were dissolved in acetonitrile (105 cm³) and irradiated according to method(i). The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as eluant, and was run for fourteen-and-a-half hours. The solvent was removed in vacuo, and the reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to chloroform. The first fraction was unreacted N-methylthiophthalimide (0.78g) and the second was N-methylphthalimide (27mg, 14%). The third fraction was a major product fraction, and the fourth a minor product fraction. This latter was separated twice further by column chromatography, using chloroform as the eluant in each case, and one pure product was isolated and recrystallised from absolute ethanol. The third fraction was separated further by column chromatography using chloroform as the eluant. The major fraction from this second column was separated on a third column with chloroform as the eluant; the purest fraction from this column was recrystallised from absolute ethanol, yield 5mg. IR spectra showed that this crystalline product was the same as the other one. Total yield 10mg (~4%). No other products were purified.

Product

m.t. 137 °C. IR (1% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 2950, 1715, 1470, 1425, 1360, 1340, 1330, 1025, 735, 715, 690, 665. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 7.50-7.00 (m, 8H), 4.07 (s, 3H), 3.93 (s, 3H), 3.40 (s, 1H), 3.15 (m, 2H), 2.00-1.20 (m, ~7H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 172, 170, 142, 131.4, 130.6, 130.1, 129.5, 129.1, 127.4, 124.2, 123.5, 123.1, 122.8, 80.3, 42.1, 36.0, 32.9, 32.5, 30.7, 30.6, 30.0, 25.2, 21.5, 21.3. Found: C, 66.62; H, 6.11; N, 6.67; S, 14.78; $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_2\text{S}_2$ requires C, 66.67; H, 5.78; N, 6.22; S, 14.22%. MS m/z 240 (240.139; $\text{C}_{16}\text{H}_{18}\text{NO}$ requires 240.139), 177 (base, 177.025; $\text{C}_8\text{H}_7\text{NOS}$ requires 177.025), 117, 76, 39.

N-Methylthiophthalimide with ethyl vinyl ether

N-Methylthiophthalimide (1.00g, 0.0056 moles) was dissolved in acetonitrile (105 cm³) and nitrogen was bubbled through the solution for ten minutes. The ethyl vinyl ether (0.61g, 0.0085 moles) was then added and the solution was irradiated according to method(i), but with nitrogen being passed above the solution rather than through it, to prevent loss of ethyl vinyl ether in the nitrogen stream. Further portions (1.50g, 0.0208 moles each) of ethyl vinyl ether were added after five hours and eight-and-three-quarter hours. The reaction was monitored by T.L.C. using 1:1 chloroform:toluene as eluant, and was run for eleven hours.

After the solvent had been removed in vacuo the product mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to 4% methanol/chloroform. Four fractions were obtained, of which the first was unreacted starting material (0.46g). The second fraction consisted

of N-methylphthalimide (30mg, 6%). The third fraction was a mixture, which included a large (estimated >60% from $^1\text{H-NMR}$) proportion of N-methylphthalimide; this was in too small a quantity to give pure products when it was separated further. The fourth fraction was a mixture for which the spectral details are given below. This was separated further by column chromatography, using chloroform as the eluant, to yield one major and one minor fraction. Both fractions were impure, and the minor fraction was too small to separate further, but the major fraction was subjected to recrystallisation both from absolute ethanol, and from ethyl acetate/60-80 petrol ether, but no pure products were obtained.

Fourth fraction (mixture)

IR (oil smear) $\bar{\nu}/\text{cm}^{-1}$: 2990, 1725, 1615, 1500, 1475, 1425, 1360, 1245, 1210, 1090, 1040, 1000, 950, 910, 780, 755, 730, 690. $^1\text{H-NMR}$ (90MHz, CDCl_3) δ/ppm : 9.30-8.60 (m, 1H), 8.00-6.75 (m, 10H), 6.30-5.75 (m, $\frac{1}{2}\text{H}$), 5.30 (m, $\frac{1}{2}\text{H}$), 5.05 (m, $\frac{1}{2}\text{H}$), 4.30 (m, $\frac{1}{2}\text{H}$), 3.92(s), 3.87(s) (together 4H), 3.30 (m, 4H), 3.06(s), 3.04(s) (together 2H), 2.32(s, $\frac{1}{2}\text{H}$), 2.14(s) and 2.08(s) (total $2\frac{1}{2}\text{H}$), 1.26 (t, $J = 7\text{Hz}$, 3H), 0.60 (m, $1\frac{1}{2}\text{H}$). $^{13}\text{C-NMR}$ (90MHz, CDCl_3) δ/ppm : 168.1, 131.6, 131.3, 131.2, 130.3, 129.8, 129.4, 129.1, 128.8, 125.4, 125.1, 124.9, 124.5, 124.1, 123.3, 123.1, 121.7, 82.6, 82.1, 77.6, 77.3, 67.3, 64.4, 64.0, 36.7, 36.5, 34.1, 33.3, 31.3, 30.9, 30.3, 29.7, 28.9, 28.0, 15.1, 14.4.

N-Methylthiophthalimide with cyclohexene

N-Methylthiophthalimide (1.00g, 0.0056 moles) and cyclohexene (0.23g, 0.0028 moles) were dissolved in acetonitrile (105 cm^3) and irradiated according to method(i); the reaction was monitored by T.L.C., using 1:1 chloroform:toluene as eluant. The reaction was stopped after twenty-five

hours, but a ^1H -NMR spectrum of the reaction mixture showed that it had not proceeded very far (much N-methylthiophthalimide still present): further cyclohexene (0.26g, 0.0032 moles) was added and the reaction mixture was irradiated for a further fourteen hours. The reaction was stopped after thirty-nine hours and the solid product which had formed was filtered off and dried, yield 28mg. However the poor quality of the IR and ^1H -NMR spectra of this product suggested that it was impure.

The volatiles were removed from the soluble products in vacuo, and the reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to 6% methanol/chloroform, to give eight fractions. The first was a mixture of unreacted N-methylthiophthalimide with N-methylphthalimide (the ratio of the integrations of the NMe absorptions in the ^1H -NMR is 3:1 N-methylthiophthalimide:N-methylphthalimide, indicating that this fraction contains 48mg unreacted N-methylthiophthalimide and 17mg N-methylphthalimide) and the second was N-methylphthalimide. Crude yield of N-methylphthalimide, 185mg (21%). The third fraction contained a mixture of products, including some N-methylphthalimide. The seventh and eighth fractions contained mixtures of products, but these were smaller and less pure, as seen by ^1H -NMR and T.L.C., than the fourth, fifth and sixth fractions.

The fourth fraction was separated further on another column, using 1:1 chloroform:toluene as eluant, to give five minor and one major fractions. This major fraction was partially characterised whilst impure; attempts to recrystallise it from absolute ethanol led to decomposition. The characterisation is given below. Crude yield 28mg (2%).

The fifth fraction was separated further on another column, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to 100% chloroform. Three minor and two major fractions were obtained. The larger, purer, major fraction was recrystallised from absolute ethanol after addition of water, yield 191mg (16%) crude, 43mg (4%) pure. The other major fraction could not be recrystallised.

The sixth fraction was separated further on another column, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to 100% chloroform. Six fractions were obtained, of which two appeared to be relatively pure products, crude yields 162mg (14%) and 50mg (4%); the respective characterisations of these fractions are given below. Neither could be successfully recrystallised from absolute ethanol, even after the addition of water.

5,6-Tetramethylene-1,4-dithiane-2,3-bis(spiro-3'-2',3'-dihydro-1H-isoindol-1'-one) - first isomer (2% product)

IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 3440, 2930, 1700, 1465, 1410, 1350, 1030, 1020, 965, 755, 725. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.00-7.05 (m, 8H), 3.99 (s, 6H), 3.30-2.80 (m, 2H), 2.15-1.75 (m, 6H), 1.75-1.15 (m, 4H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 168.2, 142.1, 133.8, 131.6, 131.1, 129.7, 128.9, 123.9, 122.9, 73.5, 45.7, 32.1, 31.1, 29.7, 26.5.

5,6-Tetramethylene-1,4-dithiane-2,3-bis(spiro-3'-2',3'-dihydro-1H-isoindol-1'-one second isomer (4% product)

m.t. 237-239 °C. IR (1.5% K Br disc) $\bar{\nu}/\text{cm}^{-1}$: 2934, 1699, 1469, 1420, 1415, 1354, 1054, 1043, 1017, 990, 951, 756, 732, 687. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.90 (m, 1H), 7.90-7.50 (m, 5H), 7.25 (m, 1½H), 6.90 (t, J = 8Hz, 1H), 6.15 (d, J = 8Hz, 1H), 4.00(m) and 3.94(s), together 4½H, 3.04 (s, 3H), 2.20-1.40 (m, 10H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 169, 168, 148, 142, 131.0,

129.8, 129.4, 125.3, 124.5, 124.0, 123.5, 85, 47.9, 46.8, 31.9, 31.7, 28.1, 16.3, 26.0. Found: C, 66.33; H, 6.26; N, 6.12; S, 13.68; $C_{24}H_{24}N_2O_2S_2$ requires C, 66.03; H, 5.50; N, 6.42; S, 14.69%. MS m/z 354 (354.046; $C_{18}H_{14}N_2O_2S_2$ requires 354.050), 290 (290.106; $C_{18}H_{14}N_2O_2$ requires 290.106), 177 (base), 117, 107.

Sixth fraction - first product

IR (CCl_4) $\bar{\nu}/cm^{-1}$: 2943, 1719, 1471, 1419, 1378, 1352, 1048, 1023, 822, 730, 719. 1H -NMR (90 MHz, $CDCl_3$) δ/ppm : 9.15 (m, $\frac{1}{2}H$), 8.60 (m, 1H), 8.05-7.10 (m, 11H), 6.90 (t, $J = 8$ Hz, 1H), 6.45 (d, $J = 8$ Hz, $\frac{1}{2}H$), 6.15 (d, $J = 8$ Hz, $\frac{1}{2}H$), 4.30 (m, 1H), 3.75 (s, $\frac{1}{2}H$), 3.45 (m, 2H), 3.05 (s) and 3.04 (s), together 4H, 2.06 (s) and 2.04 (s), together 6H, 2.35-0.60 (m, 16H).

^{13}C -NMR (90 MHz, $CDCl_3$) δ/ppm : 168.9, 168.0, 143.6, 133.8, 131.8, 130.4, 129.5, 129.0, 127.6, 123.9, 123.2, 81.6, 42.1, 38.6, 25.6, 25.8, 25.4, 20.7, 20.2, 19.1.

Sixth fraction - second product

IR (CCl_4) $\bar{\nu}/cm^{-1}$: 3038, 2942, 1718, 1473, 1419, 1379, 1354, 1259, 1217, 1035, 910, 822, 728. 1H -NMR (90 MHz, $CDCl_3$) δ/ppm : 8.60 (m, 1H), 7.95-7.10 (m, 9H), 6.90 (t, $J = 8$ Hz, 1H), 6.45 (d, $J = 8$ Hz, 1H), 4.20 (m, 1H), 3.48 (s, 2H), 3.04 (s on m, 6H), 2.06 (s) and 2.04 (s), (together 4H), 2.35-0.60 (m, 14H).

^{13}C -NMR (90 MHz, $CDCl_3$) δ/ppm : 131.8, 130.5, 130.3, 129.5, 129.3, 124.1, 124.0, 123.9, 123.3, 123.2, 44.1, 40.8, 26.6, 26.1, 20.7, 19.3.

N-Methylthiophthalimide with styrene

N-Methylthiophthalimide (1.00g, 0.0056 moles) and styrene (0.35g, 0.0034 moles) were dissolved in benzene (105 cm^3) and irradiated according to method (i). A further portion of styrene (0.36g, 0.0035 moles) was added after twenty-two hours. The reaction was monitored by T.L.C., using 1:1 chloroform:

toluene and 5% methanol/chloroform as eluants, and it was stopped after forty-four hours. The solvent was removed in vacuo, and the reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to 6% methanol/chloroform, to give thirteen fractions. The first was unreacted N-methylthiophthalimide (27mg), and the second was N-methylphthalimide (33mg, 3%). Of the remaining fractions the sixth, seventh and tenth were the largest and appeared to be the most pure, as seen by $^1\text{H-NMR}$, but all of the fractions contained mixtures of products.

The sixth fraction was separated on a further column, using chloroform as the eluant, to give six fractions of which the second was the largest and the most pure, as seen by $^1\text{H-NMR}$. This sample was recrystallised from absolute ethanol to give 5-phenyl-1,4-dithiane-2,3-bis(spiro-3'-2',3'-dihydro-1'H-isoindol-1'-one) (first isomer) as off-white crystals, yield 58mg (4%).

The seventh fraction was separated on a further column, using chloroform as the eluant, to give three fractions. Attempted recrystallisation of the first fraction using ethanol/water was unsuccessful, but the second fraction was recrystallised from absolute ethanol to give 5-phenyl-1,4-dithiane-2,3-bis(spiro-3'-2',3'-dihydro-1'H-isoindol-1'-one) (second isomer) as off-white crystals, yield 173mg (14%).

The tenth fraction was separated on a further column, using chloroform as the eluant, to give four fractions. Recrystallisation of the second, third and fourth fractions using ethanol/water was attempted, but only the third gave a solid product, yield 12 mg. This was found to be impure, as seen by the $^1\text{H-NMR}$ spectrum.

5-Phenyl-1,4-dithiane-2,3-bis(spiro-3'2',3'-dihydro-1'H-isoindol-1'-one) - first isomer

m.t. 264-268 °C, turns orange upon melting. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 3385, 2971, 1696, 1613, 1597, 1499, 1470, 1452, 1418, 1370, 1034, 1022, 969, 797, 757, 728, 702, 684, 606. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 7.60-7.20 (m, 8H), 7.20-7.00 (m, 3H), 6.85 (m, 2H), 4.50 (m, 1H), 4.03 (d, $J = 11$ Hz, $1\frac{1}{4}\text{H}$), 3.65 (s, 3H), 3.61 (s, 3H), 3.55 (d, $J = 11$ Hz, $\frac{1}{2}\text{H}$). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 169.0, 168.5, 141.7, 141.1, 134.9, 131.8, 131.7, 129.6, 129.2, 128.7, 127.7, 127.1, 124.3, 123.3, 122.9, 122.7, 88, 84.6, 50.0, 35.6, 29.7, 29.2.

Found: C, 69.85; H, 5.64; N, 5.69; $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2$ requires C, 68.12; H, 4.80; N, 6.12%. MS m/z 290 ($\text{M-C}_8\text{H}_8\text{S}_2$), 249 (base, 249.114; $\text{C}_{17}\text{H}_{15}\text{NO}$ requires 249.115), 158, 117, 91.

5-Phenyl-1,4-dithiane-2,3-bis(spiro-3'-2',3'-dihydro-1'H-isoindol-1'one) - second isomer

m.t. 259-267 °C, turns orange upon melting. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 3446, 2947, 1696, 1611, 1469, 1415, 1355, 1046, 765, 739, 703, 683. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ/ppm : 8.46 (m, 1H), 8.07 (m, 1H), 7.90-7.40 (m, 8H, probably includes impurity), 7.15-6.70 (m, 8H, probably includes impurity), 4.73 (dd, $J = 9$ Hz, 11 Hz, 1H), 4.43 (m, $\frac{1}{4}\text{H}$, impurity), 4.10 (m, $\frac{1}{2}\text{H}$, impurity), 4.00 (dd, $J = 11$ Hz, 12 Hz, 1H), 3.89 (dd, $J = 9\text{Hz}$, 12 Hz, 1H), 3.83 (m, $\frac{1}{2}\text{H}$ impurity), 3.63 (s, 1H, impurity), 3.55 (s, $\frac{1}{2}\text{H}$, impurity), 3.11 (d, $J = 5$ Hz, $1\frac{1}{2}\text{H}$, impurity), 2.17 (s, 3H), 2.05 (s, 3H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 168.7, 167.9, 150.2, 142.1, 134.4, 132.2, 131.8, 130.9, 130.1, 129.8, 129.4, 129.1, 128.4, 128.1, 127.8, 127.4, 125.2, 124.2, 123.9, 123.2, 81.7, 80.7, 46.2, 31.9, 29.0, 27.7. Found: C, 71.67; H, 5.17; N, 6.17; $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2$ requires C, 68.12; H, 4.80. N, 6.12%. MS m/z 290 ($\text{M-C}_8\text{H}_8\text{S}_2$), 249 (base, 249.115; $\text{C}_{17}\text{H}_{15}\text{NO}$ requires 249.115), 158, 117, 91.

Product from tenth fraction

m.t. 214-224 °C, turns orange upon melting. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 3462, 3059, 2951, 1713, 1613, 1596, 1498, 1470, 1454, 1418, 1357, 1243, 1189, 1024, 965, 789, 753, 732, 700. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.30 (m, 3H), 8.00-6.10 (m, 15H), 5.50 (m, $1\frac{1}{2}\text{H}$), 4.75 (m, 1H), 4.30 (m, $\frac{1}{2}\text{H}$), 3.60 (m, 2H), 3.47 (s, $\frac{1}{2}\text{H}$), 3.35 (s, $\frac{1}{2}\text{H}$), 3.10 (s) and 3.00 (s), together 2H, 2.05 (m, $\frac{1}{2}\text{H}$), 1.25 (s, 2H).

N-(4-Phenylbut-3-enyl)thiophthalimide

N-(4-Phenylbut-3-enyl)thiophthalimide (1.00g, 0.0034 moles) was dissolved in dichloromethane (440 cm^3) and irradiated according to method (iii), with the cut-off of the filter solution being $\sim 480\text{nm}$. The reaction was followed by T.L.C., using 1:1 chloroform:toluene and 5% methanol/chloroform as eluants, and was stopped after forty-one-and-a-half hours. The solvent was removed in vacuo, and the reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to 4% methanol/chloroform to give six fractions. The first was unreacted N-(4-phenylbut-3-enyl)thiophthalimide (0.16g) and the second was N-(4-phenylbut-3-enyl)phthalimide (crude yield 97mg, 12%). The following fractions contained mixtures of products; the purest fraction was fourth, which was recrystallised from absolute ethanol to give off-white crystals of product, yield 48mg (6%).

10b-Mercapto-1-phenyl-1,4,6,10b-tetrahydropyrido[2,1-a]isoindol-6-one

m.t. 174-175 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 3066, 3034, 2846, 2527, 1694, 1653, 1613, 1492, 1470, 1447, 1404, 1379, 1283, 1258, 1154, 1078, 997, 803, 758, 694. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ/ppm : 7.90 (m, 1H), 7.55-7.35 (m, 5H), 7.35-7.20 (m, 2H), 7.00 (m, 1H), 6.10 (m, 1H), 5.85 (m, 1H), 4.80 (m, 1H), 3.99 (m, 1H), 3.65 (broad s, 1H), 2.05 (s, 1H). $^{13}\text{C-NMR}$ (300 MHz,

CDCl₃) δ /ppm: 164.7(s), 149.1(s), 133.4(s), 131.4, 130.3, 130.2(s), 129.9, 128.2, 128.0, 125.0, 124.2, 123.1, 69.4(s), 52.2(d), 37.8(t)
Found: C,72.49; H,5.02; N,4.63; S,10.61; C₁₈H₁₅NOS requires C,73.72; H,5.12; N,4.79; S,10.92%. MS^{m/z} 293 (M⁺, 293.087; C₁₈H₁₅NOS requires 293.087), 258 (base, 258.089; C₁₈H₁₂NO requires 258.092), 228, 202, 182, 130, 129, 115, 77.

N-(4-Phenylbut-3-enyl) dithiophthalimide

N-(4-Phenylbut-3-enyl) dithiophthalimide (0.27g, 9×10^{-4} moles) was dissolved in dichloromethane (440 cm³) and irradiated according to method (iii), with the cut-off of the filter solution being ~ 475 nm. The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as the eluant, and was stopped after fifty-three-and-a-half hours. The solvent was removed in vacuo, and the reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the eluant, to give ten small fractions. However ¹H-NMR spectra of these fractions suggested that all were impure, and IR spectra of the first eight showed the presence of oxidation products (strong C=O absorption at 1 722 cm⁻¹ or 1 723 cm⁻¹ for all of these fractions).

N-Methylthiophthalimide with acrylonitrile

N-Methylthiophthalimide (0.80g, 0.0045 moles) was dissolved in acetonitrile (105 cm³) and nitrogen was bubbled through for ten minutes. Freshly distilled acrylonitrile (1.60g, 0.0045 moles) was added and the irradiation was carried out according to method (i), but with nitrogen being passed above the solution rather than being bubbled through it. The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as eluant, and further portions of acrylonitrile (1.60g, 0.0300 moles each) were added after four, six, twelve and twenty hours. The reaction was stopped after twenty-eight hours. The solvent was removed in vacuo and the reaction

mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant, and then gradually increasing the polarity to chloroform. The first fraction consisted of unreacted starting material (0.41g). The second fraction consisted of N-methylphthalimide (11mg, 3%). The third fraction was small (5mg) and impure, and the fourth was larger (68mg) and impure. Further purification of this fraction by column chromatography, with chloroform as the initial eluant and gradually increasing the polarity to 4% methanol/chloroform did not lead to pure isolated products.

N-Methylthiophthalimide with methyl acrylate

N-Methylthiophthalimide (1.00g, 0.0056 moles) was dissolved in acetonitrile (105 cm³), and freshly distilled methyl acrylate (2.61g, 0.0300 moles) was added. Nitrogen was bubbled through the solution prior to irradiation periods, and was passed across the top during the irradiation. The irradiation was carried out according to method(i), and was monitored by T.L.C., using 1:1 chloroform:toluene as eluant. Further additions of methyl acrylate (1.70-1.85g) were made after twelve, nineteen, twenty-six, thirty-three, forty and forty-seven hours. The reaction was stopped after fifty hours. The solvent was removed in vacuo and the reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to 4% methanol/chloroform, to give nine fractions. The first was small and impure, containing unreacted N-methylthiophthalimide with a product; the second was unreacted N-methylthiophthalimide (0.19g); the third was N-methylphthalimide (24mg, 3%). All of the remaining fractions were seen by ¹H-NMR to contain mixtures of products. The

fifth was recrystallised from absolute ethanol to give white crystals (12mg), but could not be purified further; limited spectral data were obtained for this product (product 1). The sixth was recrystallised from absolute ethanol to give white crystals (29mg), some of which was lost during the recrystallisation (this is product 2). The ninth fraction was recrystallised from absolute ethanol to give white crystals (6mg); the mother liquor from this recrystallisation was evaporated in vacuo, and the residue was recrystallised from ethyl acetate/60-80 petroleum ether to give white crystals (27mg). IR spectra of both lots of crystals showed them to be identical (total yield 33mg, this is product 3). The fourth, seventh and eighth fractions were treated in the same way as the ninth, but did not give pure products.

Fourth fraction

IR (oil smear) $\bar{\nu}/\text{cm}^{-1}$: 1730, 1440, 1390, 1225, 1050, 760, 695.
 $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.00-7.15 (m, 4H), 4.55 (m, $\frac{1}{3}\text{H}$), 3.80 (m, $1\frac{1}{2}\text{H}$), 3.57 (s, $\frac{3}{4}\text{H}$), 3.40-2.80 (m including two s's, $5\frac{1}{2}\text{H}$), 2.15 (m, $\frac{3}{4}\text{H}$). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 168, 133.9, 132.2, 131.6, 130.0, 129.3, 124.4, 123.1, 122.8, 122.2, 53.1, 52.5, 51.7, 46.2, 44.0, 29.7, 24.8, 21.1, 18.7.

Fifth fraction (product 1)

IR (1% KBr disc of crystalline material) $\bar{\nu}/\text{cm}^{-1}$: 1745, 1715, 1600, 1470, 1415, 1355, 1260, 1170, 1035, 965, 750, 720, 685.
 $^1\text{H-NMR}$ (90 MHz, CDCl_3 , after recrystallisation) δ/ppm : 7.80-7.20 (m, 4H), 5.20 (dd, $J = 4 \text{ Hz}, 14 \text{ Hz}, \frac{1}{2}\text{H}$), 4.25 (m, $\frac{1}{2}\text{H}$), 3.99 (s) and 3.98 (s) (together $2\frac{1}{4}\text{H}$), 3.84 (s, 2H), 3.40 (dd, $J = 4 \text{ Hz}, 15 \text{ Hz}, \frac{2}{3}\text{H}$). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3 , sample before being recrystallised) δ/ppm : 141.8, 131.9, 130.2, 130.1, 124.1, 123.9, 123.2, 53.5, 42.8, 31.1, 29.2.

5-Methoxycarbonyl-1,4-dithiane-2,3-bis(spiro-3'-2',3'-dihydro-1'H-isoindol-1'-one) - first isomer (sixth fraction, product 2)
m.t. 207-209 °C. IR (1% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1725, 1710, 1615, 1475, 1430, 1365, 1355, 1315, 1245, 1165, 1040, 1035, 970, 760, 745, 715, 685. ¹H-NMR (90 MHz, CDCl_3) δ/ppm : 7.50-7.00 (m, 8H), 4.40 (m, $\frac{1}{2}\text{H}$), 4.20 (d, $J = 3 \text{ Hz}$, $\frac{1}{2}\text{H}$), 4.11 (s, 3H), 4.03 (s, 3H), 3.40 (m, 1H), 3.18 (s, 3H), 2.95 (d, $J = 3 \text{ Hz}$, 1H). ¹³C-NMR (90 MHz, CDCl_3) δ/ppm : 168, 166, 132.6, 132.2, 131.9, 131.3, 130.2, 125.3, 124.9, 123.6, 122.9, 122.0, 121.3, 121.0, 120.3, 68, 52.6, 48.9, 34.0, 32.7, 30.9, 28.2. Found: C, 60.04; H, 4.64; N, 6.32; S, 14.54; $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_4\text{S}_2$ requires C, 60.00; H, 4.55; N, 6.36; S, 14.55%. MS m/z 290 (290.105; $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2$ requires 290.106), 263, 230, 177 (base), 158, 117, 102, 76.

5-Methoxycarbonyl-1,4-dithiane-2,3-bis(spiro-3'-2',3'-dihydro-1'H-isoindol-1'-one) - second isomer (ninth fraction, product 3)
m.t. Turns orange at 190 °C, melts at 198-199 °C. IR (1% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1710, 1470, 1430, 1360, 1330, 1255, 1210, 1175, 1035, 750, 725, 695, 680. ¹H-NMR (90 MHz, CDCl_3) δ/ppm : 9.75 (d, $J = 7 \text{ Hz}$, 1H), 7.80-7.50 (m, 4H), 7.25 (t, $J = 8 \text{ Hz}$, 1H), 6.85 (dt, $J = 1 \text{ Hz}$, 8 Hz, 1H), 5.80 (d, $J = 8 \text{ Hz}$, 1H), 4.40 (m, 2H), 3.99 (s, 3H), 3.34 (s, 3H), 3.20 (m, 2H), 3.00 (s, 3H). ¹³C-NMR (90 MHz, CDCl_3) δ/ppm : 168.8, 131.4, 131.0, 130.4, 130.3, 129.8, 127.9, 124.0, 123.7, 52.6, 46.3, 32.7, 31.3, 28.4. Found: C, 58.58; H, 4.57; N, 6.21; S, 14.21%. MS m/z 290 ($\text{M}^+ - \text{C}_4\text{H}_6\text{O}_2\text{S}_2$, 290.104; $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2$ requires 290.106), 263, 230, 177 (base), 172, 158, 117, 76.

N-Methylthiophthalimide with methyl acrylate at low temperature

N-Methylthiophthalimide (1.00g, 0.0056 moles) was dissolved in acetonitrile (105 cm^3); the solution was cooled by a

cardice/acetone bath. Freshly distilled methyl acrylate (0.10g, 0.0012 moles) was added, and the irradiation was carried out according to method (i). The temperature of the bath was checked at least every two hours, and was maintained between -55°C and -5°C . The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as eluant, and was run for fifty-five-and-a-half hours. The solvent was removed in vacuo. Both ^1H -NMR and IR spectra of the crude reaction mixture showed only unreacted N-methylthiophthalimide together with N-methylphthalimide.

N-Methylthiophthalimide with diphenylethyne

N-Methylthiophthalimide (1.00g, 0.0056 moles) and diphenylethyne (1.50g, 0.0084 moles) were dissolved in benzene (105 cm^3) and irradiated according to method (i). The reaction was monitored by T.L.C., using both 1:1 chloroform:toluene and 5% methanol/chloroform as eluants to observe major and minor product formation respectively. It was run for twenty-two hours. The solvent was removed in vacuo and the mixture was separated by column chromatography, with 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to 4% methanol/chloroform. Five fractions were obtained, of which the first was unreacted diphenylethyne (1.34g), the second was unreacted N-methylthiophthalimide (0.79g), and the third was N-methylphthalimide (13mg, 7%). The fourth fraction was the major product fraction (crude yield 300mg), which was recrystallised from absolute ethanol to give the pure spirothiete product as pale yellow crystals (220mg, 52%). A further crop of crystals (5mg, 1%) was obtained from the mother liquor; these proved to be green, and of a different composition. The fifth fraction was small and impure, and no pure products could be isolated from it.

2-Methyl-3',4'-diphenyl-2,3-dihydro-1H-isoindole-3-spiro-2'-thiet-1-one

m.t. 153-157 °C. IR (1% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1715, 1495, 1470, 1445, 1420, 1370, 1290, 1080, 1035, 770, 750, 740, 715, 685.

$^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.35-6.90 (m, 14H), 3.08 (s, 3H).

$^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 168.1, 143.7, 132.8, 132.5, 131.3, 130.2, 129.4, 128.7, 128.0, 127.3, 125.5, 123.9, 122.1, 78.0, 25.3. Found: C, 77.71; H, 4.80; N, 3.72; S, 9.36;

$\text{C}_{23}\text{H}_{17}\text{NOS}$ requires C, 77.72; H, 4.79; N, 3.94; S, 9.02%. MS m/z 355 (M^+ , 355.103; $\text{C}_{23}\text{H}_{17}\text{NOS}$ requires 355.103), 354, 326, 322, 278, 246, 178 (base), 121, 117, 77, 76.

Variable temperature $^1\text{H-NMR}$ spectra of spirothiete

A $^1\text{H-NMR}$ spectrum run at 323 K was identical to that above, which was run at 300 K. Neither changes in chemical shifts nor additional absorptions were observed.

2-Methyl-4',5'-diphenyl-2,3-dihydro-1H-isoindole-3-spiro-3'-(1',2'-dithiol)-1-one

m.t. 193-194 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1715, 1470, 1370, 1130, 1035, 930, 805, 760, 740, 705, 690. $^1\text{H-NMR}$ (360 MHz, CDCl_3) δ/ppm (impure): 7.95-6.60 (m, 29H), 3.33 (s, 1H), 3.20 (s, $\frac{1}{3}\text{H}$), 3.15 (s, 3H), 3.08(s) and 3.07(s), (together 1H), 2.97 (s, $\frac{1}{2}\text{H}$), 1.65 (broad s, 2H).

Found: C, 71.58; H, 4.64; N, 3.60; $\text{C}_{23}\text{H}_{17}\text{NOS}_2$ requires C, 71.32; H, 4.42; N, 3.61%. MS m/z 387 (M^+ , 387.076; $\text{C}_{23}\text{H}_{17}\text{NOS}_2$ requires 387.075), 371, 354, 323 (base), 322, 246, 178, 165, 130, 105, 77, 76, 45, 31.

Second irradiation of N-methylthiophthalimide with diphenylethyne

N-Methylthiophthalimide (1.00g, 0.0056 moles) and diphenylethyne (1.47g, 0.0083 moles) were dissolved in benzene

(105 cm^3) and irradiated according to method (i) for twenty-two hours. After irradiation the solvent was removed in vacuo and ^1H -NMR and IR spectra were taken of the crude reaction mixture. The former showed unreacted N-methylthiophthalimide together with the major product in a 3:2 mole ratio; however slight shifts were noted in the positions of the N-methyl absorptions, which were at 3.28 and 3.04 ppm respectively in the 90 MHz, CDCl_3 spectrum. Comparison of the IR spectrum with those of N-methylthiophthalimide and the major product showed that all of the strong absorptions were accounted for by either or both of the two compounds, as were all of the medium-intensity absorptions, excepting one at 1157 cm^{-1} .

N-Methyldithiophthalimide with diphenylethyne

N-Methyldithiophthalimide (1.06g, 0.0055 moles) and diphenylethyne (1.47g, 0.0083 moles) were dissolved in benzene (105 cm^3) and irradiated according to method (i). The reaction was monitored by T.L.C. with 1:1 chloroform:toluene as eluant, and was run for five hours. The solvent was removed in vacuo and the products were separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually proceeding to 4% methanol/chloroform. Methanol was used as a final eluant. Five fractions were obtained. The first was largely unreacted starting materials, together with an oxidation product (IR shows a strong $\text{C}=\text{O}$ absorption at 1740 cm^{-1}); the second contained an oxidation product (IR shows $1745\text{ cm}^{-1}(\text{s})$), as did the third (IR shows $1740\text{ cm}^{-1}(\text{s})$), fourth (IR shows $1745\text{ cm}^{-1}(\text{s})$, $1730\text{ cm}^{-1}(\text{s})$) and fifth (IR shows $1745\text{ cm}^{-1}(\text{s})$, $1720\text{ cm}^{-1}(\text{s})$, $1710\text{ cm}^{-1}(\text{s})$): consequently no further work was carried out on these fractions. A yellow product remained at the top of the column; this could not be

removed either by methanol or by concentrated sodium hydroxide solution.

N-Methylthiophthalimide with phenylethyne

1) N-Methylthiophthalimide (1.02g, 0.0058 moles) and phenylethyne (0.88g, 0.0086 moles) were dissolved in acetonitrile (105 cm³) and irradiated according to method (i). The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as eluant, and was stopped after one hour as a precipitate appeared to have formed. The solid was filtered and dried, and was shown by IR to be N-methylthiophthalimide. The solvent was removed from the solution in vacuo, and IR and ¹H-NMR spectra of the residue also showed only unreacted N-methylthiophthalimide.

2) N-Methylthiophthalimide (0.50g, 0.0028 moles) and phenylethyne (2.90g, 0.0284 moles) were dissolved in benzene (105 cm³) and irradiated according to method (iii), but with the capacity of the outer jacket of the reaction vessel being 120 cm³. The cut-off of the CuCl₂/CaCl₂/HCl filter solution was around 360 nm. The reaction was run for six hours, but T.L.C., using 1:1 chloroform:toluene as eluant, showed no sign of product formation.

N-Methyldithiophthalimide with phenylethyne

N-Methyldithiophthalimide (1.00g, 0.0052 moles) was dissolved in benzene (105 cm³); nitrogen was bubbled through the solution for five minutes. Phenylethyne (0.88g, 0.0086 moles) was added and the irradiation was carried out according to method (i), but with nitrogen being passed above the solution rather than through it. The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as eluant. A further portion of phenylethyne (0.81g, 0.0079 moles) was added after

two hours, and the reaction was stopped after four hours. A ^1H -NMR spectrum of the reaction mixture showed unreacted starting materials together with a singlet of low integration at 3.45 ppm. IR of the reaction mixture showed mainly unreacted starting materials, together with a strong C=O absorption at 1733 cm^{-1} .

N-Methylthiophthalimide with hex-3-yne

N-Methylthiophthalimide (0.69g, 0.0039 moles) was dissolved in acetonitrile (105 cm^3). Nitrogen was bubbled through the solution for ten minutes, and then hex-3-yne (0.69g, 0.0084 moles) was added. The solution was irradiated according to method (i) but with nitrogen being passed above, rather than bubbled through, the solution. The reaction was monitored by T.L.C. with 1:1 chloroform:toluene as the eluant. Further portions of hex-3-yne were added after two and four hours (0.75g and 0.42g respectively). The reaction was stopped after six hours and the solvent was removed in vacuo. The reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually proceeding to chloroform. Six fractions were obtained, of which the first was unreacted N-methylthiophthalimide (0.34g), and the second was N-methylphthalimide (81mg, 25%). The following three fractions all contained products, and the sixth was too small and impure for further purification. The third fraction was recrystallised from ethanol/methanol/water to yield product 1 as yellow crystals (28mg, 5%).

The fourth and fifth fractions were both mixtures of products: these were separated further by column chromatography, using 1:1 chloroform:toluene proceeding to 5:3 chloroform:toluene and 1:1 chloroform:toluene as the respective eluants

Both columns yielded the same major slightly impure product; this could not be recrystallised from absolute ethanol, even after the addition of methanol and water, and so it was characterised in an impure state (this is product 2, yield 206 mg, 40%).

Product 1

m.t. 59-60 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 2970, 1703, 1631, 1609, 1598, 1466, 1448, 1433, 1417, 1379, 1360, 1322, 1243, 1199, 1091, 1048, 1009, 990, 931, 801, 759, 700. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 7.90-7.30 (m, 4H), 2.98 (s, 3H), 2.53 (q, $J = 8\text{Hz}$, 2H), 1.65 (q, $J = 8\text{Hz}$, 2H), 1.25 (t, $J = 8\text{Hz}$, 3H), 0.70 (t, $J = 8\text{Hz}$, 3H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 132.5, 130.2, 125.5, 123.6, 25.3, 24.2, 20.6, 14.8, 14.6.

Found: C, 61.48; H, 5.72; N, 4.68; S, 23.78; $\text{C}_{15}\text{H}_{17}\text{NOS}_2$ requires C, 61.86; H, 5.84; N, 4.81; S, 21.99%. MS m/z 291 (M^+ , 291.074; $\text{C}_{15}\text{H}_{17}\text{NOS}_2$ requires 291.075), 258 (base), 226, 198, 178, 115, 81.

Product 2

IR (oil smear) $\bar{\nu}/\text{cm}^{-1}$: 2973, 2935, 1714, 1469, 1424, 1369, 1129, 1070, 1028, 748. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.10-7.05 (m, 4½H), 3.40 (m, ½H), 2.96 (s, 2½H), 2.65 (q, $J = 8\text{Hz}$, 2H), 1.85 (q, $J = 8\text{Hz}$, 2H), 1.70 (m, ½H), 1.35 (t, $J = 8\text{Hz}$, 3H), 1.20 (m, 1½H), 0.78 (t, $J = 8\text{Hz}$, 3H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 167, 132.6, 131.8, 131.6, 130.9, 130.3, 123.9, 123.3, 122.1, 25.1, 18.6, 14.2, 13.3, 12.9. MS m/z 259 (M^+ , 259.102; $\text{C}_{15}\text{H}_{17}\text{NOS}$ requires 259.103), 227, 198 (base), 184, 170, 146, 104, 76.

N-Methyldithiophthalimide with hex-3-yne

N-Methyldithiophthalimide (1.00g, 0.0052 moles) was dissolved in acetonitrile (105 cm^3). Nitrogen was passed through the solution for ten minutes and then hex-3-yne

(0.84g, 0.010 moles) was added. The irradiation was carried out according to method (i), but with nitrogen being passed across the top of the solution rather than being bubbled through. The reaction was monitored by T.L.C. using 1:1 chloroform:toluene as eluant. Further portions of hex-3-yne were added after three and seven hours (0.85g and 0.71g respectively). The reaction was stopped after ten-and-a-half hours and the solvent was removed in vacuo. The reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to chloroform. Methanol was used to elute the final fraction. The first fraction was unreacted N-methyldithiophthalimide (0.89g), and the remaining fractions all contained oxidised products as seen by their IR spectra, all of which showed strong carbonyl absorptions.

N-Methyldithiophthalimide with dimethyl acetylenedicarboxylate

N-Methyldithiophthalimide (1.00g, 0.0052 moles) was dissolved in acetonitrile (105 cm³). Nitrogen was passed through the solution for ten minutes and dimethyl acetylenedicarboxylate (1.12g, 0.0079 moles) was added. Nitrogen was passed across the top of the solution during the irradiation. Further dimethyl acetylenedicarboxylate (0.88g, 0.0062 moles) was added after four hours. The reaction was monitored by T.L.C. using 1:1 chloroform:toluene as the eluant, and was stopped after eight hours. The IR and ¹H-NMR spectra which were taken of the reaction mixture suggested that products had been formed: the former shows a strong C=O absorption at 1 728 cm⁻¹ (this could also be N-methylphthalimide, however), and the latter shows additional (i.e. to N-methyldithiophthalimide) NMe absorptions at 3.41, 3.14, 3.06 and 2.33 ppm. An absorption

at 3.47 ppm may arise from N-methylthiophthalimide or from the methyl groups on the esters.

N-Methylthiophthalimide with bis(methylthio)ethyne

N-Methylthiophthalimide (0.50g, 0.0028 moles) and bis(methylthio)ethyne (0.67g, 0.0056 moles) were dissolved in dichloromethane (105 cm^3), and the solution was irradiated according to method (iii), with the cut-off of the filter solution $\sim 360\text{nm}$. The reaction was followed by T.L.C., using 1:1 chloroform:toluene as the eluant, and was stopped after five-and-a-half hours. The solvent was removed in vacuo and a ^1H -NMR spectrum was taken of the reaction mixture. From the ratios of the integrations of the N-methyl absorptions of N-methylthiophthalimide and the products, it was estimated that at least 56% of the N-methylthiophthalimide had reacted. The reaction mixture was separated by column chromatography, using 175g of 0.40-0.10mm silica, with 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to 6% methanol/chloroform. One main product fraction was obtained. This was recrystallised from absolute ethanol to give red crystals (334mg, 72%). Although the crystalline product appears to be in one form (sharp melting point), both E and Z forms of the compound are seen in solution.

2-Methyl-3-{methylthio[(methylthio)thiocarbonyl]methylene}-2,3-dihydro-1H-isoindol-1-one

m.t. $105-109^\circ\text{C}$. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1715, 1555, 1470, 1445, 1425, 1365, 1340, 1300, 1185, 1155, 1090, 1045, 1000, 940, 760, 735, 705, 690, 670, 650. Found: C, 52.95; H, 4.58; N, 4.69; S, 33.02; $\text{C}_{13}\text{H}_{13}\text{NOS}_3$ requires C, 52.88; H, 4.44; N, 4.74; S, 32.55%. IR (CH_2Cl_2) $\bar{\nu}/\text{cm}^{-1}$: 1715(s), 1600(m),

1575(m), 1475(m), 1425(m), 1365(m), 1090(s), 1035(s), 1010(s), 800(s). MS m/z 295 (M^+), 248, 233, 216(base), 201, 117.

E-form (37% in solution)

$^1\text{H-NMR}$ (90 MHz, CDCl_3) δ /ppm: 7.85-7.15 (m, 4H), 3.68, (s, 3H), 2.72 (s, 3H), 2.30 (s, 3H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ /ppm: 228.2, 167.8, 136.4, 134.6, 131.6, 129.0, 128.7, 123.0, 122.0, 121.5, 31.1, 21.0, 17.6.

Z-form (63% in solution)

$^1\text{H-NMR}$ (90 MHz, CDCl_3) δ /ppm: 8.85 (dd, $J = 2 \text{ Hz}, 8 \text{ Hz}$, 1H), 7.85-7.15 (m, 3H), 3.21 (s, 3H), 2.69 (s, 3H), 2.08 (s, 3H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ /ppm: 227.8, 167.7, 137.8, 136.7, 132.3, 129.7, 129.0, 125.8, 124.1, 123.2, 29.7, 20.4, 17.4.

Variable-temperature $^1\text{H-NMR}$ spectra showed:-

Temperature (K)	<u>E</u> (% in solution)	<u>Z</u> (% in solution)
300	35	65
314	33	67
328	33	67

N-Methyldithiophthalimide with bis(methylthio)ethyne

N-Methyldithiophthalimide (1.00g, 0.0052 moles) and bis(methylthio)ethyne (0.61g, 0.0052 moles) were dissolved in acetonitrile (440 cm^3); the solution was irradiated according to method (iii), with the filter solution cut-off at 480 nm approx. The reaction was monitored by T.L.C. using 1:1 chloroform:toluene as eluant, and was run for twenty-nine hours. The solvent was removed in vacuo, and a $^1\text{H-NMR}$ spectrum was taken which showed that approximately 56% of the N-methyldithiophthalimide had reacted (this was estimated from the integrations of the NMe absorptions of the N-methyldithioph-

thalimide and the products). The mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to chloroform. The first fraction contained unreacted starting materials, the second a mixture of N-methyldithiophthalimide with the major products, and the third the major products; lower R_f fractions contained small quantities of impure material. The second fraction was separated further by column chromatography, using 1:1 chloroform:toluene as the initial eluant, gradually increasing the polarity to chloroform, to give an N-methyldithiophthalimide fraction, which was added to the first fraction of the original column, and a major product fraction, which was added to the third fraction of the original column. The first fraction was recrystallised from ethyl acetate to give pure N-methyldithiophthalimide (0.13g). The third fraction was recrystallised from absolute ethanol to give slightly impure dark magenta product crystals (767mg, 55%). These crystals were recrystallised again from absolute ethanol to give pure crystals (576mg, 41%).

2-Methyl-3-{methylthio[(methylthio)thiocarbonyl]methylene}-2,3-dihydro-1H-isoinidole-1-thione

m.t. 104-106 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1470, 1455, 1425, 1340, 1315, 1195, 1155, 1130, 1085, 1030, 985, 970, 935, 905, 765, 660, 635. Found: C, 50.24; H, 4.22; N, 4.48; S, 39.34; $\text{C}_{13}\text{H}_{13}\text{NS}_4$ requires C, 50.16; H, 4.21; N, 4.50; S, 41.16%. MS m/z 311 (M^+ , 310.992; $\text{C}_{13}\text{H}_{13}\text{NS}_4$ requires 310.993), 264, 232 (base), 217, 185, 146.

E-form (37% in solution)

$^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.15-7.15 (m, 4H), 4.22 (s, 3H), 2.82 (s, 3H), 2.39 (s, 3H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm :

226.4, 192.1, 140.0, 138.1, 134.8, 133.2, 132.7, 126.4, 125.1, 123.3, 36.6, 21.1, 17.0.

Z-form (63% in solution)

$^1\text{H-NMR}$ (90 MHz, CDCl_3) δ /ppm: 8.85 (dd, $J = 2, 8$ Hz, 1H), 8.15-7.15 (m, 3H), 3.70 (s, 3H), 2.78 (s, 3H), 2.40 (s, 3H).

$^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ /ppm: 226.4, 192.1, 136.4, 136.2, 131.9, 131.3, 129.9, 129.1, 125.6, 125.1, 35.4, 20.7, 17.2.

N-Methylthiophthalimide with bis(t-butylthio)ethyne

N-Methylthiophthalimide (1.00g, 0.0056 moles) and bis(t-butylthio)ethyne (1.20g, 0.0059 moles) were dissolved in acetonitrile (440 cm^3) and irradiated according to method (iii), with the cut-off of the filter solution being 480 nm approx. The reaction was monitored by 1:1 chloroform:toluene and was run for twenty-two hours. The solvent was removed in vacuo and the mixture was separated by column chromatography. The first fraction was unreacted alkyne, the second was unreacted N-methylthiophthalimide, the third was the major product fraction, the following fraction was small and impure, and the final fraction appeared (by $^1\text{H-NMR}$) to be an impure product fraction. This latter could not be purified further by recrystallisation from absolute ethanol, and as the $^1\text{H-NMR}$ spectrum had shown it to be a poor quality sample, it was not subjected to further work. The first fraction was recrystallised from ethyl acetate to give pure N-methylthiophthalimide (360mg). The major product fraction was recrystallised from absolute ethanol to yield a mixture of red crystals and yellow crystals. These were separated manually as far as possible. $^1\text{H-NMR}$ and IR spectra of the yellow crystals showed them to be N-methylphthalimide. The red crystals were recrystallised again to give pure product crystals (339 mg, 25%).

2-Methyl-3-{*t*-butylthio[(*t*-butylthio)thiocarbonyl]methylene}-2,3-dihydro-1*H*-isoindol-1-one

m.t. 93-95 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 2950, 1715, 1545, 1470, 1455, 1420, 1360, 1335, 1245, 1165, 1090, 1035, 1005, 945, 770, 720, 695. ¹H-NMR (90 MHz, CDCl₃) δ/ppm : 9.10 (m, 1H), 7.90-7.30 (m, 3H), 3.42 (s, 3H), 1.67 (s, 9H), 1.50 (broad s, 9H). ¹³C-NMR (90 MHz, CDCl₃) δ/ppm : 234.0, 168.2, 137.9, 134.0, 132.0, 129.9, 126.5, 123.3, 122.0, 52.9, 51.3, 31.2, 30.4, 28.1, 26.4. Found: C, 60.07; H, 6.78; N, 3.75; S, 25.26; C₁₉H₂₅NOS₃ requires C, 60.16; H, 6.60; N, 3.69; S, 25.33%. MS m/z 379 (M⁺, 379.111; C₁₉H₂₅NOS₃ requires 379.110), 258, 233, 202(base), 190, 117, 57, 41.

N-Methylthiophthalimide with N-(*p*-tolyl)diphenylketenimine

N-Methylthiophthalimide (0.50g, 0.0028 moles) and N-(*p*-tolyl)diphenylketenimine (0.80g, 0.0028 moles) were dissolved in dichloromethane (440 cm³) and irradiated according to method (iii), with the cut-off of the filter solution at 360 nm approx. The reaction was monitored by T.L.C. using 1:1 chloroform:toluene and 5% methanol/chloroform as eluants, and was run for two-and-a-half hours. The solvent was removed in vacuo, and a ¹H-NMR spectrum of the reaction mixture showed that the reaction had almost gone to completion. The mixture was separated by column chromatography on 0.4-0.1 mm silica, using 3% methanol/dichloromethane as the eluant. One major product fraction was obtained, which was recrystallised from absolute ethanol to give white crystals (214mg, 76%).

2-Methyl-3',3'-diphenyl-4'-*p*-tolylimino-2,3-dihydro-1*H*-isoindole-3-spiro-2'-thietan-1-one

m.t. 183-184 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 2930, 1715, 1665, 1650, 1600, 1505, 1495, 1460, 1450, 1420, 1370, 1255, 1065,

1035, 855, 815, 800, 745, 725, 705, 685, 645. $^1\text{H-NMR}$ (90 MHz, CCl_4) δ /ppm: 7.85 (d, $J = 8\text{Hz}$, 1H), 7.75 (m, 1H), 7.55-6.90 (m, 15H), 6.50 (d, $J = 8\text{Hz}$, 1H), 2.65 (s, 3H), 2.40 (s, 3H). $^{13}\text{C-NMR}$ (200 MHz, CDCl_3) δ /ppm: 168.0, 160.2, 144.9, 144.5, 140.8, 140.6, 135.7, 131.1, 130.6, 130.0, 129.2, 128.8, 128.6, 128.2, 127.9, 127.6, 127.3, 127.2, 126.7, 125.6, 123.0, 120.5, 81.3, 78.1, 26.9, 20.9. Found: C, 78.14; H, 5.28; N, 5.97; S, 7.02; $\text{C}_{30}\text{H}_{24}\text{N}_2\text{OS}$ requires C, 78.23; H, 5.25; N, 6.08; S, 6.96%. MS m/z 461 ($(\text{M}+\text{H})^+$), 311, 301, 283, 177, 165 (base), 152, 133, 117, 91, 77.

N-Methyldithiophthalimide with N-(p-tolyl)diphenylketenimine

N-Methyldithiophthalimide (0.50g, 0.0026 moles) and N-(p-tolyl)diphenylketenimine (0.73g, 0.0026 moles) were dissolved in dichloromethane (440 cm^3) and irradiated according to method (iii), with the filter solution cut-off being at 360 nm approx. The reaction was monitored by T.L.C. using 1:1 chloroform:toluene as the eluant, and was run for four-and-a-half hours. The solvent was removed in vacuo, and a $^1\text{H-NMR}$ spectrum was taken: this showed that the reaction had virtually gone to completion. The reaction mixture was separated by column chromatography, on 0.4-0.1 mm silica, using 2% methanol/chloroform as the eluant. One major product fraction was obtained, which was recrystallised from absolute ethanol to give yellow crystals.

2-Methyl-3',3'-diphenyl-4'-p-tolylimino-2,3-dihydro-1H-isoindole-2'-thietane-1-thione

m.t. 145-148 $^{\circ}\text{C}$. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1670, 1650, 1505, 1490, 1475, 1445, 1435, 1375, 1335, 1315, 1130, 1060, 1010, 855, 800, 790, 765, 742, 717, 695, 690, 640. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ /ppm: 9.05 (d, $J = 8\text{Hz}$, 1H), 7.80-6.90 (m, 16H), 6.30 (d,

$J = 8\text{Hz}, 1\text{H}), 3.04 (\text{s}, 3\text{H}), 2.41 (\text{s}, 3\text{H})$. $^{13}\text{C-NMR}$ (200 MHz, CDCl_3) δ/ppm : 193.5, 159.6, 144.6, 141.2, 140.6, 140.3, 137.1, 136.0, 132.1, 131.0, 130.7, 130.1, 129.7, 128.8, 128.6, 128.3, 128.2, 128.1, 127.7, 127.3, 126.9, 126.4, 124.8, 124.4, 122.9, 120.5, 83.4, 82.0, 32.5, 20.9. Found: C, 75.63; H, 5.39; N, 5.70; S, 13.43; $\text{C}_{30}\text{H}_{24}\text{N}_2\text{S}_2$ requires C, 75.60; H, 5.07; N, 5.88; S, 13.45%. MS 476 (M^+), 327, 283, 193, 165(base), 146, 117, 89, 65.

N-Methylthiophthalimide with diphenylketene

N-Methylthiophthalimide (0.80g, 0.0045 moles) was dissolved in dichloromethane (440 cm^3). The solution was cooled to -10°C , using a cardice/acetone bath, and diphenylketene (1.75g, 0.0090 moles) was added. The irradiation was carried out according to method (iii), with the filter solution cut-off being at about 360 nm. The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as eluant, and was run for fifty-four hours. The solvent was removed in vacuo and a $^1\text{H-NMR}$ spectrum was run on the reaction mixture, which showed that approximately 92% of the N-methylthiophthalimide had reacted, to give mainly two products in an estimated 1:2 ratio (1:2 $\delta 2.90$: $\delta 2.64$; the proportions of N-methylthiophthalimide and products were calculated from the relative integrations of the NMe absorptions). The reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to chloroform. Nine fractions were obtained, of which the first contained unreacted starting materials, the following four unreacted starting materials mixed with products, the sixth was mainly the major product, the seventh was a mixture of major and minor products, the eighth was minor product and the ninth was a small impure fraction. Both the sixth and eighth

fractions were recrystallised from absolute ethanol. The latter yielded off-white crystals of diphenylmethylen product. The former gave white needles of the thietane product mixed with off-white crystals. The two were separated manually. Yield of thietane product 393mg (26%). Total yield of of diphenylmethylen product 122mg (9%). The diphenylmethylen product was characterised by comparison with the product obtained from the reaction of N-methylthiophthalimide with 1,1-diphenylethene.

2-Methyl-3',3'-diphenyl-2,3-dihydro-1H-isoindole-3-spiro-2'-thietane-1,4'-dione

m.t. 149-151 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1755, 1702, 1495, 1475, 1450, 1420, 1370, 1255, 1090, 1055, 1035, 1000, 810, 800, 790, 755, 725, 705, 690, 675, 640. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 7.90 (d, $J = 8\text{Hz}$, 1H), 7.55-6.90 (m, 12H), 6.50 (d, $J = 8\text{Hz}$, 1H), 2.64 (s, 3H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 181.5, 168.0, 144.0, 138.9, 138.8, 131.4, 131.0, 130.7, 129.7, 128.9, 128.5, 128.2, 127.9, 127.8, 127.6, 125.8, 123.4, 75.4, 27.4. Found: C, 74.85; H, 4.50; N, 3.78; S, 8.55; $\text{C}_{23}\text{H}_{17}\text{NO}_2\text{S}$ requires C, 74.37; H, 4.58; N, 3.77; S, 8.63%. MS m/z 311 ($\text{M}^+ - \text{COS}$, 311.132; $\text{C}_{22}\text{H}_{17}\text{NO}$ requires 311.131, base), 194, 165, 91, 60. UV $\lambda_{\text{max}}/\text{nm}$; 349 ($\epsilon = 1200 \text{ l mol}^{-1} \text{ cm}^{-1}$).

Irradiation of thietane product

The thietane product (20mg, 5×10^{-5} moles) was dissolved in d_6 -benzene (2 cm^3 approx.) and placed in a 5mm NMR tube under a nitrogen atmosphere. The tube was attached to the Pyrex filter of a 400W medium-pressure mercury arc and irradiated. The reaction was monitored by $^1\text{H-NMR}$, and the thietane product was seen (by the positions of the -NMe absorptions) to be cleanly and quantitatively converted to the diphenylmethylen

product in two hours. The solvent was removed in vacuo, the sample was dried, and a KBr disc IR spectrum showed it to be pure diphenylmethylenes product.

Thermal decomposition of the thietane product

The thietane product ($\sim 10\text{mg}$) was dissolved in absolute ethanol ($\sim 1.5\text{ cm}^3$) and placed in a Pyrex test-tube. A second sample was similarly prepared, but with the addition of a few crystals of benzenesulphonic acid. The two samples were heated at 80°C in a water-bath for two hours. The sample without acid showed a slight colour change to yellow, but did not appear different on T.L.C. (1:1 chloroform:toluene) from an unheated sample. The acid sample had become yellow, and this, together with T.L.C., suggested that one of the decomposition products might be N-methylthiophthalimide. Both samples had the solvent removed in vacuo, and the acid sample was dissolved in chloroform and washed three times with concentrated sodium hydrogen carbonate solution. The chloroform solution was dried over anhydrous magnesium sulphate, and finally the chloroform was removed in vacuo. A ^1H -NMR spectrum of the sample without acid showed some decomposition to N-methylthiophthalimide, but mainly to the diphenylmethylenes product; the ^1H -NMR spectrum of the acid sample gave a similar spectrum. The ratio of diphenylmethylenes product to N-methylthiophthalimide was about 9.2:1.0 for the acid sample and 4.0:1.0 for the sample without acid.

N-Methyldithiophthalimide with diphenylketene

N-Methyldithiophthalimide (0.80g, 0.0041 moles) was dissolved in dichloromethane (105 cm^3). The reaction mixture was cooled in a cardice/acetone bath and nitrogen was bubbled

through before the diphenylketene (0.80g, 0.0041 moles) was added. The irradiation was carried out using a high-pressure mercury arc and a $\text{CuCl}_2/\text{CaCl}_2/\text{HCl}$ filter solution (cut-off at 360 nm approx). The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as eluant, and stopped after fifteen hours. The solvent was removed in vacuo. A ^1H -NMR spectrum of the reaction mixture showed that there were two major products, with the $-\text{NCH}_3$ ratios of N-methyldithiophthalimide to product 1 ($-\text{NCH}_3$ at $\delta 3.30$) to product 2 ($-\text{NCH}_3$ at $\delta 3.00$) being approximately 1:6:3. This suggested that 90% of the N-methyldithiophthalimide had reacted, and that the maximum product yields were 67% and 33% respectively. The reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and increasing the polarity to chloroform, to give nine mixed product fractions. The second fraction appeared to be almost pure, and ^1H -NMR showed it to contain the major products. This fraction did not prove amenable to separation on a further column, so it was recrystallised from absolute ethanol. Two components appeared to be present: some of the solid dissolved fairly readily, and some did not appear to dissolve at all. The pale yellow insoluble component was filtered off and the solution containing the soluble component was cooled to precipitate out a bright yellow solid. The insoluble solid proved to be a pure sample of the thietane product (120mg, 8%). The soluble product proved to be a slightly impure sample of the diphenylmethylene product (145mg, 12%). It was later found (see below) that the diphenylmethylene product could be purified most easily by irradiation. None of the other fractions from the initial column were purified further.

2-Methyl-3',3'-diphenyl-1-thioxo-2,3-dihydro-1H-isoindole-3-spiro-2'-thietan-4'-one

m.t. 152-153 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1750, 1595, 1495, 1475, 1452, 1432, 1362, 1320, 1135, 1100, 1060, 1025, 825, 800, 765, 760, 745, 705, 685, 642. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.07 (d, $J = 8\text{Hz}$, 1H), 7.55-7.00 (m, 12H), 6.35 (d, $J = 8\text{Hz}$, 1H), 3.03 (s, 3H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 194, 191, 138.6, 138.3, 137.3, 133.0, 131.0, 130.1, 129.0, 128.6, 128.2, 127.8, 127.5, 125.4, 125.2, 124.8, 123.2, 122.5, 80.3, 56.6, 33.0. Found: C, 71.48; H, 4.37; N, 3.70; $\text{C}_{23}\text{H}_{17}\text{NOS}_2$ requires C, 71.29; H, 4.42; N, 3.61%. MS m/z 327 ($\text{M}^+ - \text{COS}$, base, 327.108; $\text{C}_{22}\text{H}_{17}\text{NS}$ requires 327.108), 250, 194, 165, 146, 91, 77, 60. UV $\lambda_{\text{max}}/\text{nm}$: 403 ($\epsilon = 9\,500\text{ l mol}^{-1}\text{ cm}^{-1}$).

3-(Diphenylmethylene)-2-methyl-2,3-dihydro-1H-isoindole-1-thione

m.t. 164-165 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1490, 1475, 1465, 1445, 1360, 1345, 1135, 1085, 1020, 765, 755, 695, 620. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.05 (dd, $J = 2\text{Hz}, 8\text{Hz}$, 1H), 7.55-7.00 (m, 12H), 6.40 (dd, $J = 2\text{Hz}, 8\text{Hz}$, 1H), 3.32 (s, 3H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 191.1, 139.8, 138.4, 136.0, 134.4, 130.2, 129.9, 128.5, 128.1, 127.9, 127.5, 123.5, 121.4, 36.1. Found: C, 80.69; H, 5.00; N, 4.24; S, 10.12; $\text{C}_{22}\text{H}_{17}\text{NS}$ requires C, 80.70; H, 5.23; N, 4.28; S, 9.79%. MS m/z 327 (M^+ , base, 327.108; $\text{C}_{22}\text{H}_{17}\text{NS}$ requires 327.108), 250, 194, 165, 146, 91, 77. UV $\lambda_{\text{max}}/\text{nm}$: 402.5 ($\epsilon = 22,000\text{ l mol}^{-1}\text{ cm}^{-1}$).

Irradiation of thietane product

The thietane product (20mg, 5×10^{-5} moles) was dissolved in d_6 -benzene (2 cm^3 approx.) and placed in a 5mm NMR tube under a nitrogen atmosphere. The tube was attached to the Pyrex filter of a 400 W medium pressure mercury arc and the sample was irradiated. The reaction was followed by $^1\text{H-NMR}$,

and the compound was seen to be converted cleanly and quantitatively to the diphenylmethylene compound. (The chemical shift of the $-NCH_3$ absorption changed from $\delta 3.00$ to $\delta 3.30$.) The solvent was removed in vacuo, the sample was dried, and a KBr disc IR spectrum showed that the solid product was the pure diphenylmethylene product.

Thermal decomposition of the thietane product

The thietane product (~ 10 mg) was dissolved in absolute ethanol ($\sim 1.5 \text{ cm}^3$) and the solution was placed in a Pyrex test-tube. A second sample was similarly prepared, but with the addition of a few crystals of benzenesulphonic acid. Both samples were heated at 80°C in a water-bath for two hours. The sample without acid showed a colour change to yellow and the appearance of some N-methyldithiophthalimide as seen by T.L.C., using 1:1 chloroform:toluene as eluant. The acid sample appeared yellow-brown and showed some N-methyldithiophthalimide on T.L.C. The solvent was removed from both samples in vacuo, and the acid sample was dissolved in chloroform and washed three times with concentrated sodium hydrogen carbonate solution. The chloroform solution was dried over anhydrous magnesium sulphate and finally the chloroform was removed in vacuo. $^1\text{H-NMR}$ spectra of the acid and without acid samples both showed decomposition to have occurred, with N-methyldithiophthalimide as the main decomposition product, and the diphenylmethylene product as a minor product. The ratio of N-methyldithiophthalimide:diphenylmethylene product was about 1.5:1.0 for the sample without acid, and about 2.1:1.0 for the acid sample.

The *N*-methylthiophthalimides with allenes

The irradiations carried out were *N*-methylthiophthalimide with *t*-butoxyallene, with α -D-*t*-butoxyallene, with isopropylthioallene, with α -D-*t*-butylthioallene and with *m*-tolylallene, and *N*-methyldithiophthalimide with *t*-butoxyallene, with α -D-*t*-butoxyallene, with α -D-*t*-butylthioallene and with *m*-tolylallene. The irradiation vessel was immersed in a cardice/acetone bath to prevent thermal reactions from occurring. In all cases the formation of products was evident from T.L.C., using 1:1 chloroform:toluene as the eluant, and from ^1H -NMR spectra of the reaction mixtures. However separation by column chromatography or by preparative H.P.L.C. did not give pure products, even though the unreacted allene had first been removed in vacuo. The reactions for which the separations were more successful, and which led to partially purified products, are described below. The thermal experiments, which gave similarly complex mixtures of products, are also described below.

N-Methylthiophthalimide with *t*-butoxyallene

N-Methylthiophthalimide (0.50g, 0.0028 moles) was dissolved in dichloromethane ($\sim 200\text{ cm}^3$) and cooled in a cardice/acetone bath for ten minutes; *t*-butoxyallene (4.50g, 0.040 moles) was then added, together with pyridine (1 cm^3). The irradiation was carried out according to method (iii), with the cut-off of the filter solution being at 360 nm approx. The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as eluant, and by visually observing the colour change, and was stopped after one hour. Most of the dichloromethane was removed in vacuo by rotary evaporation, and the excess allene was removed

in vacuo using a vacuum pump and adding three portions ($\sim 5 \text{ cm}^3$) of dichloromethane to assist the evaporation. The allene was trapped in a trap cooled in liquid nitrogen. The reaction mixture was stored under nitrogen. A ^1H -NMR spectrum was taken of the crude product mixture before it was separated by H.P.L.C., using dichloromethane as the eluant. The unreacted starting materials eluted first, followed by a fairly pure product fraction, which was characterised further, and several mixed product fractions. The fraction of greatest purity could not be recrystallised from absolute ethanol, nor from dichloromethane/hexane.

Crude reaction mixture

^1H -NMR (90 MHz, CDCl_3) δ /ppm: 7.95-7.25 (m, $4\frac{1}{3}\text{H}$), 6.10 (broad s $\frac{2}{5}\text{H}$), 5.85 (d, $J = 4\text{Hz}$, $\frac{1}{4}\text{H}$), 5.22 (t, $J = 2.4\text{Hz}$) and 5.20 (m), total $1\frac{1}{3}\text{H}$, 5.13 (t, $J = 2.4\text{Hz}$, $\frac{3}{4}\text{H}$), 5.00 (m, $\frac{2}{5}\text{H}$), 4.88 (t, $J = 2.4 \text{ Hz}$, 1H), 4.83 (m, $\frac{1}{4}\text{H}$), 4.75 (m, $\frac{1}{3}\text{H}$), 4.55 (m, $\frac{2}{5}\text{H}$), 3.25(s), 3.20(s) and 3.15(s), total $2\frac{1}{2}\text{H}$, 2.65 (m, $\frac{2}{3}\text{H}$), 2.45 (d, $J = 6\text{Hz}$, 1H), 1.45(m), 1.25(s) and 0.85(s), not integrated, and 0.05 (s, 1H). Using the hexamethyldisiloxane signal as standard it may be calculated from the N-methyl-absorptions at δ 3.25, 3.20 and 3.15 that the total amount of products is about 8×10^{-4} moles.

Product fraction

IR (CH_2Cl_2 solution) ν/cm^{-1} : 2970(m), 1710(s), 1475(m), 1375(m), 1095(s), 1055(m), 1010(s), 805(s). ^1H -NMR (90 MHz, CDCl_3) δ /ppm: 8.00-7.30 (m, 4H), 5.50 (t, $J \sim 2\text{Hz}$, 1H), 5.40 (t, $J \sim 2\text{Hz}$, 1H), 5.20 (t, $J \sim 2\text{Hz}$, 1H), 3.30 (s, 3H), 1.30 (m, 2H), probably an impurity, 0.95 (s, 9H). ^{13}C -NMR (200 MHz, CDCl_3) δ /ppm: 167.9, 145.3, 142.1, 131.7, 130.2, 129.0, 124.8, 122.9, 103.6, 81.3, 78.8, 74.7, 28.1, 25.2. MS m/z 289 (M^+), 232 (base, $\text{M}^+ - (\text{CH}_3)_3\text{C}$), 175, 146, 117, 57.

N-Methylthiophthalimide with α -D-t-butoxyallene

N-Methylthiophthalimide (0.70g, 0.0039 moles) was dissolved in dichloromethane ($\sim 400 \text{ cm}^3$) and cooled in a cardice/acetone bath for ten minutes; α -D-t-butoxyallene (0.75g, 0.0064 moles) was then added. The irradiation was carried out according to method (iii), with the cut-off of the filter solution being at 360 nm approx. The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as eluant, and by visually observing the colour change, and was stopped after two hours. The dichloromethane and excess allene were removed as described for the t-butoxyallene experiment. A ^1H -NMR spectrum was taken of the crude product mixture before it was separated by H.P.L.C., using 3% methanol/dichloromethane as the eluant. The first product fraction obtained was moderately pure, but those eluting later were all of mixed composition. The pure fraction could not be recrystallised from dichloromethane/hexane.

Crude reaction mixture

^1H -NMR (90 MHz, CDCl_3) δ /ppm: 7.95-7.05 (m, 14H), 6.85 (t, $J = 7\text{Hz}$, $\frac{1}{2}\text{H}$, unreacted allene), 6.20 (m, $\frac{1}{2}\text{H}$), 5.90 (m, $\frac{1}{2}\text{H}$), 5.65 (d, $J = 7\text{Hz}$, $\sim \frac{1}{2}\text{H}$, unreacted allene), 5.22 (d, $J = 2\text{Hz}$) and 5.18 (d, $J = 2\text{Hz}$), total 2H, 4.87 (d, $J = 2\text{Hz}$) and 4.83 (d, $J = 2\text{Hz}$), total 2H, 4.00 (s, $\frac{1}{2}\text{H}$), 3.85 (s, $\frac{1}{2}\text{H}$), 3.40 (s, $\frac{1}{2}\text{H}$), 3.25, 3.20 and 3.15 (singlets, 6H), 2.90 (s, 2H), 2.05 (m, 2H), 1.30 and 1.25 (singlets, 10H), 1.00 and 0.95 (singlets, 5H), 0.80 (s, 20H). Using the hexamethyldisiloxane signal as standard, it may be calculated from the N-methyl absorptions at 3.40, 3.25, 3.20 and 3.15 that the total amount of products formed is about 2×10^{-4} moles.

Product fraction

$^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.00-7.10 (m, 4H), 5.44 (d, $J = 2\text{Hz}$) and 5.40 (d, $J = 2.9\text{Hz}$), total 0.6H, 5.10 (d, $J = 2\text{Hz}$) and 5.04 (d, $J = 2.5\text{Hz}$) total 0.6H, 3.25, 3.15 and 3.10 (s's, 3.6H), 1.30 (s, 2H), 0.85 (s, 6H). $^{13}\text{C-NMR}$ (200 MHz, CDCl_3) δ/ppm : 165.8, 143.2, 140.0, 131.8, 130.1, 129.6, 128.2, 127.9, 127.6, 127.3, 126.9, 122.7, 121.5, 121.0, 120.8, 120.2, 101.7, 101.5, 79.1, 72.9, 72.6, 29.1, 26.7, 26.0, 24.7, 23.1, 21.8.

N-Methylthiophthalimide with isopropylthioallene

N-Methylthiophthalimide (0.50g, 0.0028 moles) was dissolved in dichloromethane ($\sim 400\text{ cm}^3$) and cooled in a cardice/acetone bath for ten minutes; isopropylthioallene (1.50g, 0.0132 moles) was then added to the reaction mixture. The irradiation was carried out according to method (iii), with the cut-off of the filter solution being at about 360 nm. The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as eluant, and by visually observing the colour change, and was stopped after two hours. The dichloromethane and excess allene were removed as described for the t-butoxyallene experiment. A $^1\text{H-NMR}$ spectrum was taken of the crude product mixture before it was separated by H.P.L.C., using dichloromethane as the initial eluant, followed by 1% methanol/dichloromethane. Five fractions were obtained, of which the first was unreacted allene, the second unreacted N-methylthiophthalimide, the fourth contained products and the fifth a small quantity of products. An attempt was made to separate the fourth fraction further on another H.P.L.C., using 3% methanol/dichloromethane as the eluant, but no pure products were obtained.

Crude reaction mixture

$^1\text{H-NMR}$ (90 MHz, CDCl_3) δ /ppm: 8.00-7.25 (m, 4H), 5.34 (t, $J = 2.7$ Hz) and 5.28 (t, $J = 2.7$ Hz), total 1H, 5.08 (s, CH_2Cl_2) and 5.05 (t, $J = 2.7$ Hz), total $\frac{1}{2}\text{H}$, 4.91 (t, $J = 2.7$ Hz) and 4.87 (t, $J = 2.7$ Hz), total 0.7H, 3.30 (s) and 3.25 (s), total 3H, 2.65 (septet, $J = 7$ Hz, 1H), 1.30 (m, 3H, impurity), 1.05 (d, $J = 7$ Hz), 0.90 (d, $J = 7$ Hz) and 0.80 (d, $J = 7$ Hz), total 5H. Using the hexamethyldisiloxane signal as standard it may be calculated from the N-methyl absorptions at 3.30 and 3.25 that the product formation is almost quantitative.

Product fraction

IR (CH_2Cl_2) $\bar{\nu}/\text{cm}^{-1}$: 2970, 1710, 1650, 1470, 1420, 1370, 1055, 855, 810, 800. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ /ppm: 8.00-7.30 (m, 4H), 5.61 (t, $J = 2.7$ Hz), 5.57 (t, $J = 2.7$ Hz) and 5.49 (t, $J = 2.7$ Hz), total 1.5H, 5.20 (t, $J = 2.7$ Hz), 5.18 (t, $J = 2.7$ Hz) and 5.13 (t, $J = 2.7$ Hz), total 1.5H, 3.35 (s) and 3.30 (s), total 3H, 2.62 (septet, $J = 7$ Hz, 1H), 1.80 (m, $\frac{1}{3}\text{H}$), 1.30 (m), 1.15 (d, $J = 7$ Hz), 1.00 (d, $J = 7$ Hz) and 0.85 (d, $J = 7$ Hz), total 6H. $^{13}\text{C-NMR}$ (200 MHz, CDCl_3) δ /ppm: 172.4, 145.5, 141.1, 139.4, 132.4, 131.9, 131.1, 129.7, 129.4, 124.1, 123.2, 123.1, 122.5, 105.3, 104.7, 63.1, 59.2, 37.0, 27.1, 25.1, 23.9, 23.5. MS m/z 291 (M^+), 233, 216, 190, 184 (base), 158, 114, 99, 77, 72.

N-Methylthiophthalimide with α -D-t-butylthioallene

N-Methylthiophthalimide (0.80g, 0.0045 moles) was dissolved in dichloromethane ($\sim 400 \text{ cm}^3$) and cooled in a cardice/acetone bath for ten minutes; α -D-t-butylthioallene (1.20g, 0.0093 moles) was then added. The irradiation was carried out according to method (iii), with the cut-off of the filter solution being at about 360 nm. The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as the eluant, and by visually observing

the colour change, and was stopped after seven hours. The dichloromethane and excess allene were removed as described for the t-butoxyallene experiment. A ^1H -NMR spectrum was taken of the crude product mixture. On standing the reaction mixture in the freezer, crystals formed. These were separated, washed with 40-60 petroleum ether and dried. This product could not be purified by further attempts at recrystallisation, using dichloromethane/hexane.

Crude reaction mixture

^1H -NMR (90 MHz, CDCl_3) δ /ppm: 8.05-6.95 (m, 12H), 6.40 (s, $\frac{1}{6}\text{H}$), 6.25 (s, $\frac{1}{6}\text{H}$), 5.45 (d, $J = 2$ Hz) and 5.40 (m), total 1H, 5.00 (d, $J = 2$ Hz) and 4.95 (m), total 1H, 4.00-3.40 (several singlets, $1\frac{1}{2}\text{H}$), 3.20 (s) and 3.15 (s), total $4\frac{1}{2}\text{H}$, 3.00 (s) and 2.95 (s), total $1\frac{2}{3}\text{H}$, 2.80 (s) and 2.75 (s), total $1\frac{2}{3}\text{H}$, 2.25 (s) and 2.20 (s), total 2H, 1.85 (d, $J = 8$ Hz, 1H), 1.55-0.35 (m, 17H). Using the hexamethyldisiloxane signal as standard it may be calculated from the N-methyl absorptions between 3.35 and 2.55 that the total amount of products formed is 1.1×10^{-3} moles.

Product crystals

^1H -NMR (90 MHz, CDCl_3) δ /ppm: 8.00-7.15 (m, 8H), 5.50 (d, $J = 2.4$ Hz, 1H), 5.05 (d, $J = 2.4$ Hz, 1H), 4.80 (s, $\frac{1}{6}\text{H}$), 3.25 (s, 2.8H), 3.00 (s) and 2.90 (s), both low integration, 2.30 (s, $\frac{1}{4}\text{H}$), 1.50-0.40 (m, 8H). ^{13}C -NMR (90 MHz, CDCl_3) δ /ppm: 165.5, 143.2, 139.9, 130.2, 129.8, 129.2, 127.6, 127.2, 121.7, 121.0, 120.4, 103.0, 102.5, 77.4, 41.5, 30.0, 29.3, 29.0, 28.6, 28.1, 24.8, 23.1.

N-Methylthiophthalimide with m-tolylallene, using a medium-pressure mercury arc

N-Methylthiophthalimide (0.80g, 0.0045 moles) was dissolved in dichloromethane (105 cm³) and nitrogen was bubbled through the solution for ten minutes; m-tolylallene (0.91g, 0.0070 moles) was added. The irradiation was carried out according to method (i). (In this case the vessel was not immersed in a cardice/acetone bath, as it had been observed in previous N-methylthiophthalimide/allene experiments that there is no dark reaction at room temperature. This was also shown by T.L.C. to be the case here.) The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as eluant, and visually by observing the colour change, and was stopped after one hour. The dichloromethane and excess allene were removed as described for the t-butoxyallene experiment. A ¹H-NMR spectrum was taken of the reaction mixture, which showed it to contain several products of which none was dominant. The reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant, and gradually increasing the polarity to 6% methanol/chloroform. Ten fractions were obtained, all of which were mixtures.

N-Methyldithiophthalimide with m-tolylallene, using a medium-pressure mercury arc

This reaction was carried out as described for the preceding experiment but with the irradiation vessel immersed in a cardice/acetone bath, using N-methyldithiophthalimide (0.60g, 0.0031 moles) and m-tolylallene (0.64g, 0.0055 moles) in dichloromethane (105 cm³). The reaction was stopped after one hour. The ¹H-NMR spectrum of the reaction mixture showed that it contained a mixture of products with none dominant.

The reaction mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually proceeding to chloroform. Nine fractions were obtained, all of which were mixtures.

Thermal reaction of *N*-methylthiophthalimide with α -D-*t*-butylthioallene

N-Methylthiophthalimide (50.3mg, 2.8×10^{-4} moles) was added to hexamethyldisiloxane solution (0.5 cm³ of a tetrachloromethane solution containing 0.94g in 100 cm³, 0.058M) and placed in a 5 mm NMR tube. The tube was placed in an atmosphere of nitrogen and α -D-*t*-butylthioallene (0.185g, 0.00144 moles) was added. The tube was sealed and placed in a thermostat at 30 °C in the dark. ¹H-NMR spectra were run at intervals between zero and twenty-four hours, but no changes were observed.

Thermal reaction of *N*-methyldithiophthalimide with α -D-*t*-butylthioallene

This reaction was carried out using the method described above, but with *N*-methyldithiophthalimide (50mg, 2.6×10^{-4} moles) and α -D-*t*-butylthioallene (0.166g, 0.00129 moles). ¹H-NMR (60 MHz) spectra were run at intervals between zero and twenty-four hours, and the ratios of the integrations for the broad singlet of the α -D-*t*-butylthioallene at δ 4.85 and the HMDS absorption at δ 0.05, and of the integrations for the product multiplets around δ 5.55 and δ 5.15 and the HMDS absorption at δ 0.05 were calculated. The results are presented below.

Time/hours	Integration ratios		
	$\delta 0.05:\delta 4.85$	$\delta 0.05:\delta 5.15$	$\delta 0.05:\delta 5.55$
0	1:1.11	1:0	1:0
1	1:0.91	1:0.17	1:0.14
3	1:0.83	1:0.22	1:0.18
5½	1:0.83	1:0.26	1:0.22
24	1:0.63	1:0.12	1:0.12

Comparison of these spectra with that from the product mixture of the photochemical reaction (described below) between N-methyldithiophthalimide and α -D-t-butylthioallene shows that in the photochemical reaction the α -D-t-butylthioallene absorption at $\delta 4.80$ disappears completely.

Thermal reaction mixture after twenty-four hours

$^1\text{H-NMR}$ (90 MHz, CCl_4) δ /ppm: 8.05-7.05 (m, 4H), 5.55 (m, $\frac{1}{2}\text{H}$), 5.15 (m, $\frac{1}{2}\text{H}$), 4.85 (s, 2H), 4.35 (m, $\frac{1}{2}\text{H}$), 4.15 (m, $\frac{1}{2}\text{H}$), 4.00 (s, $\frac{1}{2}\text{H}$), 3.65 (s) and 3.60 (s), total 2H, 3.20 (s) and 3.15 (s), total $1\frac{1}{2}\text{H}$, 2.05 (s, 4H), 1.75-1.05 (four singlets, 12H), 1.05-0.55 (five singlets, 10H), 0.05 (s, 2H).

Photochemical reaction mixture

$^1\text{H-NMR}$ (90 MHz, CDCl_3) δ /ppm: 8.05-6.75 (m, 4H), 6.05 (m, $\frac{1}{4}\text{H}$), 5.55 (m, $\frac{1}{8}\text{H}$), 5.15 (m, $\frac{1}{8}\text{H}$), 3.80 (s), 3.60 (s), 3.55 (s), 3.40 (s), 3.35 (s) and 3.15 (s), total 3H, 2.35 (s) and 2.30 (s), total $\frac{1}{2}\text{H}$, 1.80 (s, $\frac{1}{2}\text{H}$), 1.55-0.55 (several singlets, 8H).

Photochemical reaction of N-methyldithiophthalimide with α -D-t-butylthioallene

N-Methyldithiophthalimide (0.80g, 0.0041 moles) was dissolved in dichloromethane ($\sim 400\text{ cm}^3$) and placed in a large photochemical reaction vessel which was immersed in a cardice/acetone bath. Nitrogen was bubbled through the solution for

ten minutes, and then the α -D-t-butylthioallene (1.00g, 0.0077 moles) was added. The irradiation was carried out according to method (iii), with the cut-off of the filter solution at about 360 nm. The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as the eluant, and by visually observing the colour change, and was stopped after six hours. The dichloromethane and excess allene were removed as described for the N-methylthiophthalimide/t-butoxyallene experiment, and a ^1H -NMR spectrum was taken of the crude reaction mixture. Separation by H.P.L.C., using 0.5% methanol/dichloromethane as the eluant, did not lead to the isolation of pure products.

Experiments to investigate the properties of
the photoproducts

Heating 2-methyl-3',4'-diphenyl-2,3-dihydro-1H-isoindole-3-spiro-2'-thietan-1-one in acid solution

The title compound (20mg) was heated in absolute ethanol (3 cm^3) in a test-tube, and a few crystals of benzenesulphonic acid were added. A second sample was prepared, but without the acid. Both samples were heated in a water-bath at $\sim 80^\circ\text{C}$ for two hours. T.L.C., using 1:1 chloroform:toluene and 5% methanol/chloroform as eluants, did not show any differences between these samples and a sample which had not been heated. Both samples gave crystals on cooling; the crystals were filtered off, dried, and shown by IR to be unreacted thietane.

Heating 2-methyl-3',4'-diphenyl-2,3-dihydro-1H-isoindole-3-spiro-2'-thiet-1-one in acid solution - short experiment.

The title compound (15mg) was heated in absolute ethanol (3 cm^3), and a few crystals of benzenesulphonic acid were added. The sample was heated at 80°C in a water bath for

two hours. T.L.C., using 1:1 chloroform:toluene as eluant, showed the formation of two products in small quantities.

Heating 2-methyl-3',4'-diphenyl-2,3-dihydro-1H-isoindole-3-spiro-2'-thiet-1-one in acid solution - long experiment

The title compound (15mg) was placed in absolute ethanol (25 cm³), and a few crystals of benzenesulphonic acid were added. The sample was refluxed for twenty-four hours. A second sample was treated in the same way, but without the acid. The acid sample showed substantial changes on T.L.C., using 1:1 chloroform:toluene and 5% methanol/chloroform as eluants, indicating the formation of at least three products, although it did not appear to have changed colour. The solvent was removed from both samples in vacuo. The acid sample was dissolved in chloroform, washed three times with concentrated sodium hydrogen carbonate solution, dried over anhydrous magnesium sulphate and filtered; finally the chloroform was evaporated in vacuo. ¹H-NMR spectra were taken of both samples. As the sample which had been heated without acid appeared to contain mostly unreacted starting material, an IR spectrum was also taken of this sample. The sample which had been heated with acid appeared by ¹H-NMR to have decomposed (as seen by the loss of the -NMe absorption at δ 3.09) to form several products.

Heat + acid sample

¹H-NMR (90 MHz, CDCl₃) δ /ppm: 8.00-6.50 (m, 19H), 3.64 (s, $\frac{1}{3}$ H), 3.15 (s, low integration), 3.10 (s, low integration), 2.95 (s, $\frac{1}{3}$ H), 2.68 (s, 1H), 2.53(s) and 2.51(s), total 1 $\frac{1}{2}$ H, 2.35 (s, 1H), 1.65 (m, 1H), 1.25 (m, 2H), 0.90 (m, 1H).

Heat only sample

$^1\text{H-NMR}$ (90 MHz, CDCl_3) δ /ppm: 7.80-6.70 (m, 14H), 4.80 (broad s, 4H), 3.09 (s, $2\frac{1}{2}\text{H}$), 1.25 (m, 1H). IR (oil smear) $\bar{\nu}/\text{cm}^{-1}$: as for the unreacted compound, but with some of the minor absorptions less clearly defined, and with one additional absorption at 1132(m).

Melting of 2-methyl-3',4'-diphenyl-2,3-dihydro-1H-isoindole-3-spiro-2'-thiet-1-one

The title compound (20mg) was placed in a Pyrex test-tube, and heated in an oil-bath until the compound melted. It was then cooled slowly by being retained in the bath, which was left to stand overnight. T.L.C., using 1:1 chloroform:toluene and 5% methanol/chloroform as eluants, showed no change from a sample which had not been melted. A $^1\text{H-NMR}$ spectrum of the melted sample showed an increase in the impurity absorption around 1.60 ppm. $^{13}\text{C-NMR}$ and IR spectra were also taken for the melted sample. As the quantity was small, the melted sample was not purified further.

Sample before melting

$^1\text{H-NMR}$ (90 MHz, CDCl_3) δ /ppm: 8.05-6.75 (m, 14H), 3.09 (s, 3H), 1.62 (s, $\frac{2}{3}\text{H}$).

Melted sample

IR (oil smear) $\bar{\nu}/\text{cm}^{-1}$: 2930, 1715, 1495, 1470, 1440, 1415, 1370, 1285, 1150, 1135, 1120, 1100, 1080, 1035, 1025, 770, 745, 720, 690, 640. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ /ppm: 8.05-6.80 (m, 14H), 3.09 (s, 2.7H), 1.59 (s, 5H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ /ppm: 132.7, 130.4, 129.5, 129.1, 128.9, 128.2, 127.5, 125.7, 124.0, 122.3, 31.1.

Heating 2-methyl-3',3'-diphenyl-4'-p-tolylimino-2,3-dihydro-1H-isoindole-3-spiro-2'-thietane-1-thione in acid solution

The title compound (5mg) was placed in absolute ethanol (3 cm³) in a Pyrex test-tube, together with a few crystals of benzenesulphonic acid. A second sample was prepared, but without the acid. Both samples were heated in a water bath at 80 °C for two hours. The sample without acid showed no colour change, neither did it appear different from an unheated sample by T.L.C., using 1:1 chloroform:toluene as the eluant. By contrast the acid sample had become yellow in colour, and showed nine spots on T.L.C., including spots which appeared to correspond to N-methyldithiophthalimide, N-methylthiophthalimide and N-(p-tolyl)diphenylketenimine. The acid sample was dissolved in chloroform, washed three times with concentrated sodium hydrogen carbonate solution and dried over anhydrous magnesium sulphate; the solution was filtered and the solvent was removed in vacuo. A ¹H-NMR spectrum was taken.

Heat + acid sample

¹H-NMR (90 MHz, CDCl₃) δ/ppm: 8.20-6.80 (m, 59H), 6.60 (m, ½H), 6.40 (m, 1H), 5.40 (s, ½H), 5.10 (s, ½H), 5.00 (s, ½H), 3.80 (s, 1½H), 3.48 (s, 1½H), 3.32 (s, 1½H), 2.90 (m, ½H), 2.80 (s, 1½H), 2.70 (s, 1H), 2.50 (s, ½H), 2.25 (m, 10H), 0.85 (m, 5H).

Heating 2-methyl-3',3'-diphenyl-4'-p-tolylimino-2,3-dihydro-1H-isoindole-3-spiro-2'-thietan-1-one in acid solution

The title compound (5mg) was placed in absolute ethanol (1 cm³) in a Pyrex test-tube, together with a few crystals of benzenesulphonic acid. A second sample was prepared, but without the acid. Both samples were heated in a water-bath at 80 °C for two hours. The sample without acid showed no

colour change, neither did it appear different from an unheated sample by T.L.C., using 1:1 chloroform:toluene as the eluant. However the acid sample had become yellow-orange in colour, and showed six spots on T.L.C., including spots which appeared to correspond to N-methylthiophthalimide and N-(p-tolyl)diphenylketenimine. The acid sample was dissolved in chloroform, washed three times with concentrated sodium hydrogen carbonate solution and dried over anhydrous magnesium sulphate; the solution was filtered and the solvent was removed in vacuo. A ^1H -NMR spectrum was taken. Attempted column chromatography, using 1:1 chloroform:toluene as the initial eluant, and proceeding to 5:3 chloroform:toluene gave four fractions, none of which were pure and all of which contained substantial quantities of column material.

A similar reaction was carried out using chloroform as the solvent (in place of ethanol) and heating the samples at 40°C for two hours. As in the ethanol reactions, the sample without acid showed no change in colour, T.L.C. characteristics (using 1:1 chloroform:toluene as eluant) or ^1H -NMR spectrum. The acid sample showed a colour change to yellow-orange, the appearance of three product T.L.C. spots including N-methylthiophthalimide and N-p-(tolyl)diphenylketenimine, and a ^1H -NMR spectrum which indicates a mixture of products.

Heat + acid in ethanol solution

^1H -NMR (90 MHz, CDCl_3) δ /ppm: 8.00-7.00 (m, 15H), 5.05 (s, $\frac{1}{4}\text{H}$), 4.30 (m, $1\frac{1}{2}\text{H}$), 3.45 (s, 1H), 3.20 (s, $\frac{1}{4}\text{H}$), 2.30 (s, $\frac{1}{2}\text{H}$), 2.15 (s, $\frac{1}{4}\text{H}$), 2.00 (s, $\frac{1}{4}\text{H}$), 1.60 (m, 7H), 1.20 (m, 14H), 0.85 (m, $9\frac{1}{2}\text{H}$).

Heat + acid in chloroform solution

¹H-NMR (90 MHz, CDCl₃) δ/ppm: 8.00-7.40 (m, 4H), 7.40-7.00 (m, 12H), 5.05 (d, J = 6Hz, 1H), 4.20 (q, J = 8 Hz, 2H), 3.45 (s, 3H), 2.35 (m with d, J = 6Hz, 3H), 1.25 (m, 9H), 0.85 (m, 4H).

CHAPTER SEVEN

PHOTOCHEMISTRY OF THIOPHTHALIMIDES:

OTHER REACTIONS

EXPERIMENTAL

Photooxidation reactions

Photooxidation of *N*-methylthiophthalimide

N-Methylthiophthalimide (0.50g, 0.0028 moles) in acetonitrile (105 cm³ approx.) was irradiated according to method (i), but with oxygen being bubbled through the solution instead of nitrogen. The reaction was monitored by T.L.C. using 1:1 chloroform:toluene as the eluant. After four hours, when the reaction appeared to have gone to completion, the solvent was removed in vacuo. IR and ¹H-NMR spectra of the crude product showed that *N*-methylphthalimide was the only organic compound present. The crude product was recrystallised from industrial methylated spirit to give two crops of crystalline *N*-methylphthalimide (0.30g, 66%).

Determination of sulphur and of sulphur dioxide

N-Methylthiophthalimide was irradiated as described above, but the reaction was stopped after six-and-a-half hours. (This was the time taken for the reaction mixture to decolorise, and the difference between this value and the value for the above reaction is probably due to the different oxygen flow rates.) T.L.C. showed that the reaction had not gone to completion, and a ¹H-NMR spectrum run on the reaction mixture after the solvent had been removed indicated that 87% of the *N*-methylthiophthalimide had reacted.

During the irradiation the gases leaving the reaction vessel were bubbled through 0.75 M sodium hydroxide solution (100 cm³ approx.) in order to trap any evolved sulphur dioxide as sodium sulphite.^{230,231} The sulphite was partially oxidised to sulphate by the oxygen which was being passed through the solution, and also partially by standing for one day. The

solution was neutralised and then acidified slightly by the addition of concentrated hydrochloric acid, and the remaining sulphite was oxidised to sulphate by the addition of bromine. The solution was boiled to remove the excess bromine, and a boiling solution of barium chloride (3.00g, 0.0123 moles in 100 cm³ water) was added. The resulting solution was boiled for three minutes and allowed to cool to room temperature. The suspension was filtered through a preweighed grade 4 sinter for gravimetric analysis. Yield of barium sulphate = 0.011g, which is equivalent to 1.5 mg of sulphur (2% yield based on reacted N-methylthiophthalimide).

The elemental sulphur was recovered by scraping the sides of the reaction vessel and filtering the suspension: the mass of sulphur was 19 mg (48% yield based on reacted N-methylthiophthalimide).

Photooxidation of N-methylthiophthalimide : control

N-Methylthiophthalimide (0.40g) in acetonitrile (105 cm³ approx.) was placed in a photochemical reaction vessel. Oxygen was bubbled through the solution, which was kept dark by being covered with a black polythene sack. The flow of oxygen was stopped after six-and-a-half hours and the solvent was removed in vacuo. Both ¹H-NMR and T.L.C. (1:1 chloroform: toluene) showed only N-methylthiophthalimide to be present, with no trace of N-methylphthalimide.

Photooxidation of N-methyldithiophthalimide

N-Methyldithiophthalimide (1.00g, 0.0052 moles) in acetonitrile (105 cm³ approx.) was irradiated according to method (i), but with oxygen being bubbled through the solution instead of nitrogen. The progress of the reaction was

monitored by T.L.C. using 1:1 chloroform:toluene as the eluant, and also by periodically removing a sample of reaction mixture, evaporating the solvent in vacuo and taking a ^1H -NMR spectrum (the samples were redissolved and returned to the reaction vessel). The ^1H -NMR results, showing the extent of the reaction, are given in table 7.1 and figure 7.1.

Time/hours	Dithio	Monothio	Fully oxidised
0	10	0	0
12½	5.2	3.2	1.6
19½	2.9	4.2	2.9
25½	0.4	2.2	7.4
31	0	0	10

Table 7.1: Variation in relative proportions of N-methyldithio-phthalimide, N-methylthiophthalimide and N-methylphthalimide with respect to time, taken from the integrations of the N-methyl absorptions in the ^1H -NMR spectra.

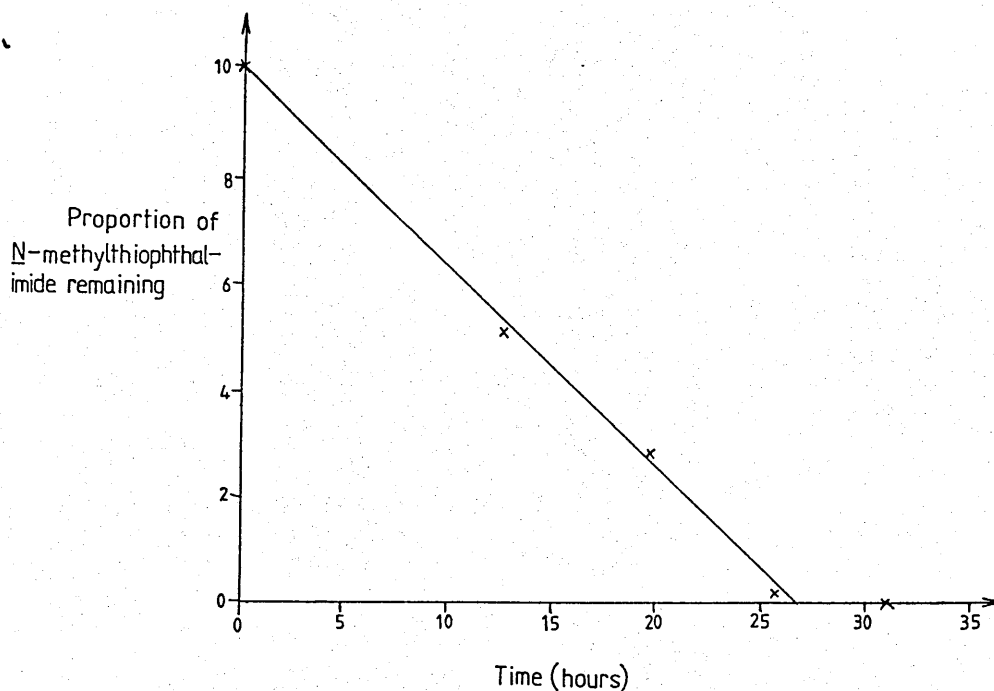


Figure 7.1: Loss of *N*-methyldithiophthalimide, taken from the integrations of the *N*-methyl absorptions in the ^1H -NMR spectra.
Rate of loss of *N*-methyldithiophthalimide = 1.9×10^{-4} moles h^{-1} under these experimental conditions.

The reaction was stopped after thirty-one hours and the solvent was removed in vacuo. IR of the crude reaction mixture showed only *N*-methylphthalimide. The crude reaction mixture was dissolved as far as possible in chloroform and filtered to remove the elemental sulphur. The chloroform was removed in vacuo, and the sample was recrystallised from ethyl acetate to give off-white needles, which were shown by IR to be *N*-methylphthalimide. Yield 0.375g (45%).

Photooxidation of *N*-methyldithiophthalimide : control

N-Methyldithiophthalimide (0.80g) in acetonitrile (105 cm^3 approx.) was placed in a photochemical reaction vessel. Oxygen was bubbled through the solution, which was kept dark

by being covered with a black polythene sack. The flow of oxygen was stopped after thirty-one hours and the solvent was removed in vacuo. Both ^1H -NMR and T.L.C. (1:1 chloroform: toluene) showed only N-methyldithiophthalimide to be present, with no trace of either N-methylthiophthalimide or N-methylphthalimide.

Hydrogen abstraction reactions

Preparations

Preparation of *N*-isobutylthiophthalimide

Thiophthalimide (4.08g, 0.0250 moles) was dissolved in DMF (25 cm³) to which ether (5 cm³) and 1-bromo-2-methylpropane (5.14g, 0.0375 moles) had been added. Anhydrous potassium carbonate (3.83g, 0.0275 moles) was added, and the solution was stirred for several hours before being left overnight. The potassium bromide was filtered off and the volatiles were removed in vacuo. The resulting red oil could not be recrystallised from 40-60 petrol ether, nor from ether, nor from ethyl acetate, and T.L.C. showed it to be a multicomponent mixture.

Separation on a silica column, with chloroform as the initial eluant and proceeding to 6% methanol/chloroform, yielded pure *N*-isobutylthiophthalimide (1.56g, 28%). IR (oil smear) $\bar{\nu}/\text{cm}^{-1}$: 2900, 1740, 1470, 1380, 1360, 1330, 1080, 1015, 770, 710, 695. ¹H-NMR (90 MHz, CDCl₃) δ/ppm : 8.20 - 7.10 (m, 4H), 3.81 (d, *J* = 7 Hz, 2H), 2.25 (m, *J* = 7Hz, 1H), 1.15 (d, *J* = 7Hz, 6H). ¹³C-NMR (90 MHz, CDCl₃) δ/ppm : 196.9, 169.6, 136.8, 133.7, 132.8, 126.9, 123.6, 122.9, 122.4, 48.0, 27.5, 20.2. Found: C, 65.12; H, 5.94; N, 6.24; S, 14.17; C₁₂ H₁₃ NOS requires C, 65.75; H, 5.94; N, 6.39; S, 14.61%.

Preparation of the *N*-*o*-tolylthiophthalimides

Phthalic anhydride (2.96g, 0.0200 moles) was heated with *o*-toluidine (2.14g, 0.0200 moles) at about 180 °C for four hours. The crude reaction product was found to be insoluble in industrial methylated spirit, and so it was heated in toluene with charcoal; the solution was filtered and cooled

to yield crystalline N-o-tolylphthalimide (2.46g, 52%).
m.t. 183-185 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1780, 1765, 1750, 1725, 1690, 1500, 1470, 1385, 1225, 1110, 885, 855, 770, 715.
 $^1\text{H-NMR}$ (60 MHz, CDCl_3) δ/ppm : 8.10 - 7.55 (m, 4H), 7.55 - 7.00 (m, 4H), 2.20 (s, 3H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 167.3, 136.5, 134.3, 132.0, 131.1, 130.6, 129.9, 129.4, 128.7, 126.8, 123.7, 18.0.

N-o-Tolylphthalimide (2.44g, 0.0103 moles) was refluxed in toluene (50 cm^3) with Lawesson's reagent (2.08g, 0.0052 moles) for five-and-a-half hours. The solvent was removed in vacuo, and the mixture was separated on a silica column using 1:1 chloroform: toluene as eluant. The fractions containing the mono- and dithio- products were evaporated in vacuo and recrystallised from toluene, to give N-o-tolylthiophthalimide (0.67g, 26%) and N-o-tolylldithiophthalimide (0.16g, 6%) as orange and purplish-brown crystals, respectively.

N-o-Tolylthiophthalimide

m.t. 112 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1745, 1500, 1470, 1370, 1310, 1225, 1170, 1130, 1075, 1025, 865, 770, 750, 715, 700. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.40 - 7.70 (m, 4H), 7.70 - 7.10 (m, 4H), 2.15 (s, 3H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 196.8, 169.2, 137.1, 136.7, 134.3, 133.5, 132.9, 131.9, 131.0, 130.5, 130.2, 129.7, 129.0, 127.6, 127.1, 126.9, 124.1, 123.7, 123.2, 17.8. Found: C, 71.07; H, 4.25; N, 5.49; S, 12.89; $\text{C}_{15}\text{H}_{11}\text{NOS}$ requires C, 71.12; H, 4.35; N, 5.53; S, 12.65%.

N-o-Tolylldithiophthalimide

m.t. 152-154 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1610, 1500, 1470, 1365, 1310, 1280, 1155, 1085, 855, 795, 770, 640, 665, 625.

$^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.10 - 7.60 (m, 4H), 7.60 - 6.90 (m, 4H), 2.07 (s, 3H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 197.4, 139.3, 136.9, 135.5, 135.0, 134.4, 133.4, 131.0, 129.9, 129.2, 126.9, 123.5, 17.9. Found: C, 66.74; H, 3.92; N, 5.14; S, 23.77; $\text{C}_{15}\text{H}_{11}\text{NS}_2$ requires C, 66.88; H, 4.12; N, 5.20; S, 23.79%.

Preparation of the *N*-(2-morpholinoethyl) thiophthalimides

N-(2-Chloroethyl)morpholine was prepared by dissolving *N*-(2-chloroethyl)morpholine hydrochloride (20.0g, 0.107 moles) in water, adding sodium hydrogen carbonate until the effervescence had ceased, extracting three times with diethyl ether, drying the extracts over magnesium sulphate, and then removing the ether in vacuo to give *N*-(2-chloroethyl)morpholine (15.00g, 94%). *N*-(2-Chloroethyl)morpholine (15.00g, 0.100 moles) was mixed with anhydrous potassium carbonate (6.91g, 0.05 moles) and phthalimide (14.70g, 0.100 moles). The mixture was heated to 160-180 °C for two hours and then cooled. Activated charcoal and ethanol were added; the mixture was heated, filtered and the solution cooled. The solid produced was recrystallised from ethanol to yield *N*-(2-morpholinoethyl) phthalimide (13.29g, 51%). m.t. 130-132 °C.

N-(2-Morpholinoethyl)phthalimide (1.95g, 7.5×10^{-3} moles) and Lawesson's reagent (1.50g, 3.7×10^{-3} moles) were refluxed in toluene (50 cm³) for three-and-a-half hours. The mixture was cooled, the solvent was removed in vacuo, and the mixture was separated by column chromatography, using 1:1 chloroform: toluene as eluant. The mono- and dithio- products could not at first be recrystallised from absolute ethanol, nor from ethyl acetate; they were dried in vacuo for several days. As IR showed the dithio- compound to be impure (C=O absorption at

1735 cm^{-1}), this sample was recrystallised from absolute ethanol. The crude yields of the mono- and dithio- products were 0.98g (47%) and 0.36g (16%) respectively, and that of the pure dithio- product 0.112g (5%).

N-(2-Morpholinoethyl)thiophthalimide m.t. 75-79 °C.

IR (1% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 2970, 2890, 2840, 2820, 1745, 1605, 1470, 1390, 1350, 1335, 1305, 1140, 1115, 1075, 1015, 995, 920, 870, 840, 795, 775, 705, 695. $^1\text{H-NMR}$ (60 MHz, CDCl_3) δ/ppm : 8.10 - 7.30 (m, 4H), 4.15 (t, $J = 7\text{Hz}$, 2H), 3.55 (t, $J = 4\text{Hz}$, 4H), 2.55 (m, 6H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 196.6, 169.4, 137.0, 133.9, 133.0, 127.1, 123.6, 122.5, 66.8, 55.6, 53.5, 37.8.

N-(2-Morpholinoethyl)dithiophthalimide m.t. 73-74 °C. IR

(1% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 1465, 1355, 1305, 1245, 1145, 1115, 1090, 1055, 980, 920, 865, 855, 775, 770. $^1\text{H-NMR}$ (60 MHz, CDCl_3) δ/ppm : 8.20 - 7.40 (m, 4H), 4.55 (t, $J = 7\text{Hz}$, 2H), 3.60 (t, $J = 4\text{Hz}$, 4H), 2.55 (m, 6H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 197.2, 134.8, 134.0, 133.0, 129.0, 128.2, 123.2, 66.9, 55.5, 53.9, 40.8. Found: C, 57.60; H, 5.49; N, 8.84; S, 21.38; $\text{C}_{14}\text{H}_{16}\text{N}_2\text{OS}_2$ requires C, 57.53; H, 5.48; N, 9.59; S, 21.92%.

Preparation of thiophthalimide: first method²³³

1,2-Dicyanobenzene (40.00g, 0.313 moles) was boiled with industrial methylated spirits (320 cm^3) until it dissolved: water (80 cm^3) was added and the suspension was cooled. Sodium sulphide (100g, 1.28 moles) was dissolved as far as possible in water (100 cm^3), and hydrogen sulphide was bubbled through for five to ten minutes in order to saturate the solution. The 1,2-dicyanobenzene suspension was added, and the mixture was stirred, and hydrogen sulphide was passed through for eight hours. The mixture was left to stand overnight, and then the solid was filtered. Hydrochloric acid was added to the filtrate

in order to precipitate more solid material. The solid material was washed with water and suspended in water (500 cm³) to which concentrated aqueous hydrochloric acid (80 cm³) had been added. The suspension was boiled for five minutes and then cooled, filtered and washed with water. The solid was dissolved as far as possible in toluene (400 cm³) and then filtered. The residue was dissolved in toluene (200 cm³) and filtered again. The filtrates were combined, and the volume was reduced so that thiophthalimide would crystallise out. Two crops of red, needle-like crystals of thiophthalimide were obtained (17.24g, 34%). m.t. 175-177 °C (literature²³³ m.t. is 175 °C). IR (nujol mull) $\bar{\nu}/\text{cm}^{-1}$: 3210, 1745, 1725, 1605, 1470, 1430, 1380, 1360, 1300, 1245, 1185, 1120, 1085, 765, 735, 685. ¹H-NMR (60 MHz, CDCl₃) δ/ppm : 8.15 - 7.60 (m, 4H), 2.60 (broad s, 1H). ¹³C-NMR (90 MHz, CDCl₃) δ/ppm : 134.4, 133.7, 124.0, 123.1 (quaternaries not seen). Found: C, 59.47; H, 2.92; N, 8.62; S, 20.64; C₈H₅NOS requires C, 58.90; H, 3.07; N, 8.59; S, 19.63%.

Preparation of the thiophthalimides: second method²¹⁹

Phthalimide (1.47g, 0.0100 moles) and Lawesson's reagent (4.04g, 0.0100 moles) were refluxed in toluene (120 cm³ approx.) for one-and-a-half hours. The reaction mixture was cooled to room temperature, the toluene was removed in vacuo, and the residue was separated on a silica column using 1:1 toluene:chloroform as the eluant. Pure thiophthalimide was not obtained following recrystallisation of the fraction which contained it, as there was contamination by unreacted phthalimide. The dithiophthalimide was recrystallised from glacial acetic acid to yield brown crystals (0.67g, 37%). m.t. partial melting at 195 - 200 °C and no further change up to 330 °C. IR (nujol

mull) $\bar{\nu}/\text{cm}^{-1}$: 3180, 1465, 1375, 1325, 1270, 1210, 1165, 1085, 765, 760, 650. Found: C, 53.60; H, 2.57; N, 8.06; S, 33.51; $\text{C}_8\text{H}_5\text{NS}_2$ requires C, 53.63; H, 2.79; N, 7.82; S, 35.75%.

Preparation of the Mannich bases

Thiophthalimide (2.20g, 0.0135 moles) was dissolved in industrial methylated spirit (20 cm^3). To the boiling solution was added 40% aqueous formaldehyde solution (2 cm^3), followed by the secondary amine (0.0150 moles) and further industrial methylated spirit (10 cm^3). The solution was boiled for five minutes and then cooled; the resulting orange-red solid was recrystallised from absolute ethanol. If the Mannich base came out of solution as an oil, then the sample was redissolved and cooled again.

N-(Dibenzylaminomethyl)thiophthalimide (1.46g, 29%) m.t. 107 - 108 °C. IR (nujol mull) $\bar{\nu}/\text{cm}^{-1}$: 1740, 1710, 1470, 1380, 1360, 1320, 1305, 1260, 1185, 1135, 1080, 945, 905, 860, 775, 740, 725, 710, 685. $^1\text{H-NMR}$ (60 MHz, CDCl_3) δ/ppm : 8.20-7.50 (m, 4H), 7.50 - 6.90 (m, 8H), 5.05 (s, 2H), 3.85 (s, 4H). $^{13}\text{C-NMR}$ (90 MHz CDCl_3) δ/ppm : 198.5, 170.5, 139.0, 137.1, 133.9, 133.0, 129.6, 128.5, 128.0, 127.5, 127.1, 126.8, 123.9, 123.2, 122.6, 59.6, 56.2.
Found: C, 74.58; H, 5.35; N, 7.55; S, 8.51; $\text{C}_{23}\text{H}_{20}\text{N}_2\text{OS}$ requires C, 74.19; H, 5.38; N, 7.53; S, 8.60%.

N-(1,2,3,4-Tetrahydroisoquinolin-2-ylmethyl)thiophthalimide (3.07g, 74%) m.t. 102-104 °C. IR (nujol mull) $\bar{\nu}/\text{cm}^{-1}$: 1735, 1470, 1425, 1400, 1375, 1345, 1310, 1150, 1140, 1105, 1085, 1060, 1000, 955, 935, 770, 755, 745, 720, 685. $^1\text{H-NMR}$ (60 MHz, CDCl_3) δ/ppm : 8.20 - 7.40 (m, 4H), 7.10 - 6.90 (m, 4H), 5.10 (s, 2H), 3.90 (s, 2H), 2.95 (m, 4H), $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 198.9, 170.7, 137.1, 134.4, 134.1, 133.9, 133.7, 133.2, 128.6, 127.6, 127.1, 126.5, 126.0, 125.5, 124.0, 123.5, 123.3, 122.8, 61.5, 53.4, 49.3, 29.2. Found: C, 70.25; H, 5.15; N, 9.12; S, 10.03; $\text{C}_{18}\text{H}_{16}\text{N}_2\text{OS}$ requires C, 70.13; H, 5.19; N, 9.09; S, 10.39%.

N-(Morpholinomethyl)thiophthalimide (2.30g, 65%) m.t. 92 - 94 °C. IR (nujol mull) $\bar{\nu}/\text{cm}^{-1}$: 1715, 1440, 1395, 1380, 1355, 1310, 1280, 1120, 1085, 1055, 980, 935, 880, 865, 830, 750, 700, 660, 635. $^1\text{H-NMR}$ (60 MHz, CDCl_3) δ/ppm : 8.20 - 7.30 (m, 4H), 4.90 (s, 2H), 3.65 (m, 4H), 2.70 (m, 4H). $^{13}\text{C-NMR}$ (90 MHz, CHCl_3) δ/ppm : 198.9, 170.6, 134.0, 133.2, 126.9,

123.9, 123.3, 122.7, 66.7, 61.5, 51.5. Found: C, 59.73; H, 5.35; N, 10.59; S, 12.33; $C_{13}H_{14}N_2O_2S$ requires C, 59.54; H, 5.34; N, 9.54; S, 12.21%.

N-(Piperidin-1-ylmethyl)thiophthalimide (2.83g, 80%) m.t.

74 - 76 °C. IR (nujol mull) $\bar{\nu}/\text{cm}^{-1}$: 1745, 1470, 1405, 1380, 1355, 1300, 1280, 1115, 1075, 1000, 970, 960, 900, 775, 760, 720, 690, 655. $^1\text{H-NMR}$ (60 MHz, CDCl_3) δ/ppm : 8.10 - 7.55 (m, 4H), 4.90 (s, 2H), 2.70 (m, 4H), 1.40 (m, 6H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 190.0, 170.7, 137.1, 134.0, 133.1, 127.1, 123.9, 123.2, 122.6, 62.5, 60.2, 52.6, 51.8, 26.0, 23.8. Found: C, 64.42; H, 6.21; N, 10.50; $C_{14}H_{16}N_2OS$ requires C, 64.62; H, 6.15; N, 10.77%.

N-(Dicyclohexylaminomethyl)thiophthalimide (3.35g, 70%) m.t.

96 - 97 °C. IR (nujol mull) $\bar{\nu}/\text{cm}^{-1}$: 1750, 1715, 1465, 1450, 1380, 1355, 1345, 1290, 1155, 1105, 955, 770, 715, 690. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.00 - 7.40 (m, 4H), 5.05 (s, $\frac{4}{3}\text{H}$), 4.71 (s, $\frac{2}{3}\text{H}$), 2.75 (m, 2H), 2.00 - 0.70 (m, 20H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 198.0, 170.4, 137.4, 133.7, 132.9, 127.7, 123.9, 123.1, 122.5, 58.3, 56.5, 32.7, 26.7, 26.0. Found: C, 70.74; H, 8.09; N, 7.82; S, 8.86; $C_{21}H_{28}N_2OS$ requires C, 70.79; H, 7.87; N, 7.87; S, 8.99%. M.S. m/z 356 (M^+), 273, 194 (base), 192, 180, 176 and 163; (m/z = 356.1930; $C_{21}H_{28}N_2OS$ requires 356.1922).

Irradiations

N-Methylthiophthalimide in toluene

The irradiation was carried out according to procedure (ii) with N-methylthiophthalimide (0.50g, 0.0028 moles) dissolved in toluene (440 cm^3). The reaction was followed by T.L.C.

using 5% methanol/chloroform as the eluant, and was run for half-an-hour. The toluene was removed in vacuo and the mixture was separated on a silica column using chloroform as the eluant. The first fraction (0.10g approx.) was mainly unreacted starting material, showing that 80% of the N-methylthiophthalimide had reacted. The second fraction contained N-methylphthalimide, as seen by $^1\text{H-NMR}$ and IR; recrystallisation of this sample gave pure crystalline N-methylphthalimide. The supernatant liquid from the recrystallisation was evaporated in vacuo and separated further by column chromatography using chloroform as the initial eluant and gradually increasing the polarity to 10% methanol/chloroform. Attempts to purify this sample further were unsuccessful, but the spectra of the impure product mixture are given below.

IR (oil smear) $\bar{\nu}/\text{cm}^{-1}$: 3470 (broad), 3040, 2940, 1765, 1710, 1615, 1600, 1495, 1470, 1455, 1435, 1385, 1255, 1205, 1105, 1040, 950, 765, 745, 720, 700. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.00 - 6.75 (m, 25H), 5.65 (s, $\frac{1}{2}\text{H}$), 5.40 (s, 1H), 3.60 (s, 1H), 3.35 (s, $\frac{1}{2}\text{H}$), 3.15 (s, 4H), 3.10 (s), 3.05 (s), 3.00 (s) and 2.85 (s), together $9\frac{1}{2}\text{H}$. $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 133.9, 132.0, 129.5, 129.0, 128.8, 128.6, 128.5, 127.4, 127.1, 124.0, 123.5, 123.2, 123.0, 83.4, 65.9, 34.2, 31.3, 28.7, 26.8, 26.1.

N-Isobutylthiophthalimide with medium-pressure mercury arc

N-Isobutylthiophthalimide (0.50g, 0.0023 moles) was dissolved in acetonitrile (105 cm^3) and irradiated according to procedure (i); the reaction was monitored by T.L.C. using 5% methanol/chloroform as the eluant. After fifty hours, the reaction was stopped, the solvent was evaporated in vacuo, and $^1\text{H-NMR}$ and IR spectra of the resulting oil showed that there was almost no change in the composition.

N-Isobutylthiophthalimide with high-pressure mercury arc

N-Isobutylthiophthalimide (146 mg, 6.7×10^{-4} moles) was dissolved in acetonitrile (105 cm^3), and the solution was placed in a small photochemical reaction vessel with a quartz filter. The reaction was stopped after forty-eight hours, when there was some evidence of the product formation on T.L.C. (eluted in 1:1 chloroform:toluene), and the solvent was removed in vacuo. A $^1\text{H-NMR}$ (90 MHz, CDCl_3) spectrum of the product mixture showed δ/ppm : 8.20 - 7.40, (m, 4H), 4.30 (broad s, $\frac{1}{2}\text{H}$), 3.86 (d, $J = 8 \text{ Hz}$, 1H), 3.50 (d, $J = 8 \text{ Hz}$, 1H), 2.25 (m, 1H), 0.94 (d, $J = 7 \text{ Hz}$, 6H). As the main change on irradiation is the diminution of the doublet at 3.86 ppm, and the appearance of a doublet at 3.50 ppm, with no change in the multiplet at 2.25 ppm, it appears that an oxidation reaction has taken place, rather than a hydrogen abstraction. To test this idea, the sample was redissolved in acetonitrile (105 cm^3) and irradiated according to method (i) with oxygen being passed through the solution instead of nitrogen. After five-and-a-quarter hours the reaction was stopped and the solvent was removed in vacuo. A $^1\text{H-NMR}$ spectrum of the product mixture showed a drastic decrease in the doublet at 3.85 ppm and a corresponding increase in the doublet at 3.50 ppm, with other small changes: δ/ppm : 8.00 - 7.50 (m, 4H), 5.00 (broad s, 0.8 H), 3.85 (d, $J = 8 \text{ Hz}$, $\frac{1}{3}\text{H}$), 3.50 (d, $J = 8 \text{ Hz}$, $1\frac{2}{3}\text{H}$), 2.25 (m, 1H), 1.30 (m, $1\frac{1}{2}\text{H}$), 0.94 (d, $J = 7 \text{ Hz}$, $4\frac{1}{2}\text{H}$).

N-o-Tolylthiophthalimide with medium-pressure mercury arc

N-o-Tolylthiophthalimide (0.61g, 0.0024 moles) was dissolved in benzene (105 cm^3) and irradiated according to procedure (i). The reaction was monitored by T.L.C., with

1:1 chloroform:toluene as eluant. As virtually no change could be observed on T.L.C. after thirty-nine hours, the reaction was stopped. A ^1H -NMR spectrum of the reaction mixture showed the appearance of two singlets: one at 2.15 ppm, which corresponds to the methyl group in the starting material, and one of lower intensity at 2.20 ppm, which is indicative of oxidation to the corresponding imide. The ratio of the total integration of the two methyl absorptions to the integration of the aromatic absorptions is 3:8; this observation suggests that no hydrogen abstraction, which would lead to a decrease in the integration of the methyl groups, has taken place, but it would however be consistent with oxidation.

N-o-Tolylthiophthalimide with high-pressure mercury arc

N-o-Tolylthiophthalimide (0.23g, 9.2×10^{-4} moles) was dissolved in benzene (440 cm³) and irradiated according to method (iii); the cut-off of the filter solution was about 478 nm. The reaction was monitored by T.L.C. using 1:1 chloroform:toluene as eluant, and was run for fifty hours. Both IR and ^1H -NMR spectra of the product mixture showed that it contained unreacted starting material and the oxidation product.

N-o-Tolyldithiophthalimide with high-pressure mercury arc

N-o-Tolyldithiophthalimide (0.105g, 3.9×10^{-4} moles) was dissolved in benzene (440 cm³) and irradiated according to method (iii); the cut-off of the filter solution was about 480 nm. The reaction was monitored by T.L.C., using 1:1 chloroform:toluene as the eluant, and was stopped after one hundred hours. An IR spectrum of the reaction mixture showed

the presence of the oxidation products N-o-tolylthiophthalimide and N-o-tolylphthalimide (C=O absorptions at 1740 and 1730 cm^{-1}). However ^1H - and ^{13}C -NMR spectra showed that there were other products present. IR (oil smear) $\bar{\nu}/\text{cm}^{-1}$: 3450 (broad), 2930, 1740, 1730, 1600, 1495, 1465, 1360, 1310, 1280, 1220, 1160, 1125, 1075, 1040, 1020, 860, 800, 775, 750, 720, 700, 630. ^1H -NMR (90 MHz, CDCl_3) δ/ppm : 8.25 - 6.70, (m, 8H), 4.35 (m, 1H), 2.33 (s), 2.19 (s), 2.13 (s) and 2.04 (s) (3H), 2.00 - 0.50 (m, 7H). ^{13}C -NMR (90 MHz, CDCl_3) δ/ppm : 197.0, 189.5, 168.0, 134.6, 134.4, 133.4, 130.9, 129.8, 129.4, 129.2, 129.0, 128.8, 126.8, 124.2, 123.7, 123.5, 123.2, 115.3, 66.2, 35.7, 31.9, 30.2, 30.0, 29.7, 29.4, 28.8, 22.7, 19.6, 17.9, 14.1. The mixture was separated on a column using 1:1 chloroform:toluene as the eluant. Eight fractions were obtained, of which the first was unreacted starting material. The second and third fractions both contained large proportions of oxidation products (strong C=O absorptions at 1752 cm^{-1} and 1730 cm^{-1} seen for both fractions in the IR spectra; compare these values with the C=O absorptions at 1750 cm^{-1} and 1725 cm^{-1} for N-o-tolylthiophthalimide and N-o-tolylphthalimide respectively). The fourth fraction was shown by its ^{13}C -NMR and IR spectra to be N-o-tolylphthalimide. The fifth and subsequent fractions were all small in quantity and did not appear pure (^1H -NMR spectra).

N-(Piperidin-1-ylmethyl)thiophthalimide with medium-pressure mercury arc

N-(Piperidin-1-ylmethyl)thiophthalimide (2.00g, 0.0077 moles) was dissolved in acetonitrile and irradiated according to method (i). The reaction was monitored by T.L.C. using 5% methanol/chloroform as the eluant and stopped after eight

hours. The yellow precipitate was filtered off, and the filtrate was evaporated in vacuo. The remainder of the yellow precipitate was dissolved in concentrated sodium hydroxide solution and reprecipitated with glacial acetic acid, filtered, washed with water and dried. IR spectra were taken for both samples of the yellow precipitate; these were found to be identical with each other and with that of an authentic sample of β -isoindigo. Yield of β -isoindigo, 159 mg (16%).

A ^1H -NMR spectrum was taken of the soluble material; this showed the presence of a singlet at $\delta 9.20$, indicative of a thioformamide product. The mixture was separated by column chromatography, with analar chloroform as the initial eluant, gradually increasing the polarity to 10% analar methanol/chloroform, to yield nine fractions, all of which were mixtures. The thioformamide product was seen by ^1H - and ^{13}C -NMR to be the major component in the first fraction and a minor one in the following three. The second fraction was seen by IR and from its solubility properties (red component not very soluble in chloroform) to contain also thiophthalimide. The first fraction was separated on a column, using analar chloroform as eluant, to yield very slightly impure N-thioformylpiperidine, as a yellow oil, yield 106 mg (11%). The chemical shifts from the ^1H - and ^{13}C -NMR spectra were compared to the literature values²⁴² and found to be similar. A lower R_f fraction from this column was recrystallised to yield pure thiophthalimide, as seen by IR spectra, as was the second fraction from the first column. The crude yield of thiophthalimide was 372 mg (30%). None of the other fractions from either of the columns appeared by T.L.C. or ^1H -NMR to contain a major component.

N-Thioformylpiperidine

IR (oil smear) $\bar{\nu}/\text{cm}^{-1}$: 2950, 2865, 1745 (w, impurity), 1510, 1450, 1245, 1210, 1135, 1110, 1010. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 9.21 (s, 1H), 4.00 (m, 2H), 3.60 (m, 2H), 1.70 (m, 6H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 185.7, 56.5, 45.8, 26.7, 24.8, 24.2.

Preparation of β -isoindigo²⁴¹

Thiophthalimide (1.00g, 0.0061 moles) and silver powder (1.25g, 0.0116 moles) were ground in a pestle and mortar, placed in a round-bottomed flask fitted with an air condenser and heated in an oil bath at 175-190 °C for one-and-a-half hours. After cooling, the solid mixture was extracted with ethanol to remove any unchanged thiophthalimide. Concentrated potassium hydroxide solution (about 10 cm^3) was added to the solid residue. The silver sulphide was filtered off and the alkaline solution was neutralised with glacial acetic acid (testing with pH paper), causing a yellow solid to precipitate. The precipitate was separated by centrifugation and washed with water. Yield 335 mg (21%).

 β -Isoindigo

m.t. > 338 °C. IR (nujol mull) $\bar{\nu}/\text{cm}^{-1}$: 3250, 1715, 1615, 1470, 1380, 1310, 1130, 775, 750, 725, 680. $^1\text{H-NMR}$ (90 MHz, d_6 -DMSO) δ/ppm : 8.40 (d, $J = 7$ Hz, 2H), 8.00 - 7.40 (m, 6H), 2.50 (broad s, 2H). $^{13}\text{C-NMR}$ (90 MHz, d_6 -acetone) δ/ppm : 168.0, 134.9, 132.3, 128.9, 124.3, 123.1, 118.6.

N-(Piperidin-1-ylmethyl)thiophthalimide with high-pressure mercury arc

N-(Piperidin-1-ylmethyl)thiophthalimide (0.61g, 0.0024 moles) was dissolved in acetonitrile (440 cm^3) and irradiated

according to method (iii), with the cut-off of the filter solution at about 480 nm. The reaction was monitored by T.L.C., using 5% methanol/chloroform as eluant. The reaction was stopped after eight hours and the solvent was removed in vacuo. A ^1H -NMR spectrum was taken, but it appeared that the reaction had not progressed very far, and so the sample was redissolved in acetonitrile (440 cm^3) and irradiated for a further six-and-a-half hours. The solvent was removed in vacuo and another ^1H -NMR spectrum was taken. Both T.L.C. and ^1H -NMR showed that a multi-component mixture had been formed. The ^1H -NMR spectrum also showed a singlet at $\delta 9.20$, indicating that N-thioformylpiperidine had been formed. On filtering the solution for ^1H -NMR the presence of an insoluble yellow compound was observed.

N-(Morpholinomethyl)thiophthalimide - first reaction

N-(Morpholinomethyl)thiophthalimide (2.00 g, 0.0076 moles) was dissolved in acetonitrile (440 cm^3) and irradiated according to method (ii) for five hours. The reaction was monitored by T.L.C. using 5% methanol/chloroform as eluant. The yellow precipitate product was filtered off and dried. IR showed it to be β -isoindigo. Yield 270 mg (27%).

The solvent was removed in vacuo from the soluble products, which were separated by column chromatography, using analar chloroform as the initial eluant and gradually increasing to 10% analar methanol/chloroform. Eight fractions were obtained. The second fraction was recrystallised twice from absolute ethanol to yield N-thioformylmorpholine as pale yellow crystals, 40 mg (4%). (The crude yield was 68%). The third fraction was separated on a further column, using analar

chloroform as the initial eluant and gradually increasing the polarity to 2% analar methanol/chloroform: one fraction, which appeared to be fairly pure as seen by T.L.C., was recrystallised from absolute ethanol to give white crystals. These were shown, by comparison of the IR, ^1H - and ^{13}C -NMR spectra with those of an authentic sample, to be N-(morpholinomethyl)-phthalimide. Yield 38 mg (3%). The fifth fraction was separated on a further column, using analar chloroform as the initial eluant and gradually proceeding to 8% analar methanol/chloroform, to yield one fraction of interest. This was recrystallised from absolute ethanol to give a pale yellow solid 3 mg, 1%. (Partial characterisation had been carried out before recrystallisation. In retrospect, following work on the second run of this experiment (see later), this was assigned as the spiro-product.

N-Thioformylmorpholine

m.t. 65-67 °C. IR (CHCl_3) $\bar{\nu}/\text{cm}^{-1}$: 2970, 2850, 1510, 1435, 1250, 1230, 1110, 1065, 1025, 915, 850, 625. ^1H -NMR (220 MHz, CDCl_3) δ/ppm : 9.27 (s, 1H), 4.10 (t, $J = 6$ Hz, 2H), 3.75 (m, 6H). ^{13}C -NMR (90 MHz, CDCl_3) δ/ppm : 187.0 (d), 66.9 (t), 66.1 (t), 55.0 (t), 45.6 (t). MS m/z 131 (base, M^+ , 131.0405; $\text{C}_5\text{H}_9\text{NOS}$ requires 131.0375), 100, 88, 73, 45, 32.

N-(Morpholinomethyl)phthalimide

IR (CHCl_3) $\bar{\nu}/\text{cm}^{-1}$: 1775, 1715, 1605, 1470, 1310, 1270, 1115, 1055, 1005, 735, 710. ^1H -NMR (90 MHz, CDCl_3) δ/ppm : 8.05 - 7.30 (m, 4H), 4.62 (s, 2H), 3.70 (t, $J = 5$ Hz, 6H), 2.66 (t, $J = 5$ Hz, 2H). ^{13}C -NMR (90 MHz, CDCl_3) δ/ppm : 134.3, 132.3, 66.9, 59.5, 50.9, 29.7.

N-(Morpholinomethyl)thiophthalimide - second reaction

N-(Morpholinomethyl)thiophthalimide (2.00 g, 0.0076 moles) was dissolved in acetonitrile (440 cm³) and irradiated according to method (ii) for six hours. The reaction was monitored using T.L.C. with 5% methanol/chloroform as eluant. This was then repeated, such that a total of 4.00g (0.0153 moles) of N-(morpholinomethyl)thiophthalimide was irradiated. In each case the yellow precipitate was dissolved in concentrated sodium hydroxide solution, reprecipitated using glacial acetic acid, and washed with water. Comparison of the IR spectrum with that of a standard sample prepared independently showed it to be β -isoindigo, yield 956 mg (48%).

The soluble material was separated by column chromatography with analar chloroform as the initial eluant, and gradually increasing the polarity to 12% analar methanol/chloroform, to yield a large number of mixed fractions. ¹H-NMR spectra were taken of all these fractions before further purification. The second fraction was separated on a further column to yield two fractions of interest, the first a mixture of thiophthalimide with N-thioformylmorpholine, and the second N-thioformylmorpholine. The first fraction from this column was recrystallised to yield thiophthalimide, 50 mg (2%). This second fraction was recrystallised to yield pure, yellow, crystalline N-thioformylmorpholine; this product was also obtained from recrystallisation of the third fraction of the original column, total yield 415 mg (21%). Recrystallisation of the ninth and eleventh fractions from the original column yielded very slightly impure samples of the pale-yellow spiro-product, yield 208 mg (7%). This was characterised in the impure form, and then recrystallised for a further, complete spectral study.

No other fraction from the original column appeared by T.L.C. or by $^1\text{H-NMR}$ to consist largely of a single component.

Spiro-product/either 3-morpholino-2,3,5,10-tetrahydroisoindolo-[1,2-b]thiazole-1-spiro-3'-(2',3'-dihydro-1'H-isoindole)-1',5-dione or 2-morpholino-9,10-dihydro-4H-isoindolo[2,1-c]thiazole-10-spiro-3'-(2',3'-dihydro-1'H-isoindole)-1',4-dione

m.t. This compound does not melt below 328°C , but it undergoes a series of colour changes from dark-yellow (210°C) to dark-brown (328°C). IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 3450 (broad), 3240 (broad), 3870, 1715, 1690, 1610, 1470, 1370, 1295, 1275, 1205, 1150, 1120, 1015, 935, 790, 740, 690. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 8.20 - 7.00 (m, 7H), 6.66 (s, 1H), 6.30 (m, 1H), 5.65 (s, 1H), 3.80 (m, 4H), 3.15 (m, 2H), 2.70 (m, 2H), 1.80 (m, 1H). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 206.1, 205.3, 141.3, 139.8, 135.7, 135.3, 133.7, 133.4, 131.0, 130.3, 124.8, 124.4, 124.3, 122.8, 102.7 (s), 82.9 (d), 75.5 (d), 67.0 (t), 48.0 (t). Found: C, 64.11; H, 4.86; N, 10.63; S, 8.07; $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$ requires C, 64.12; H, 4.83; N, 10.69; S, 8.14%. M.S. m/z 306 ($\text{M}^+ - 87$), 262, 230 (base), 190, 117; fast-atom bombardment M.S. shows m/z 393 (M^+), 306 (base), 262, 236, 229, 180, 131.

Irradiation of spiro-product

The spiro-product (~ 20 mg, 5×10^{-5} moles) was dissolved in acetonitrile (440 cm^3) and irradiated according to method (ii) for five-and-a-half hours. The solvent was removed in vacuo and a $^1\text{H-NMR}$ spectrum was taken of the residue. This showed that for $\delta \geq 2.5$ ppm, the spectrum was identical with that of a non-irradiated sample, whereas for $0 \leq \delta \leq 2.5$ ppm, it showed only a slight increase in the aliphatic multiplets. A T.L.C. plate (5% methanol/chloroform) showed that the sample

consisted largely of one component. It appears that there is very little change to the spiro-product upon irradiation under the conditions used for N-(morpholinomethyl)thiophthalimide.

N-(Morpholinomethyl)thiophthalimide: solvent comparison

N-(Morpholinomethyl)thiophthalimide (55 mg, 2.1×10^{-4} moles) was dissolved as far as possible in toluene (12 cm³ approx.) and placed in a Pyrex test-tube. A second test-tube was set up with acetonitrile as the solvent; both tubes were attached to the cooling jacket of a 400 W medium-pressure mercury arc and nitrogen was passed over the samples. The irradiation was monitored by T.L.C., using 5% methanol/chloroform as eluant, and was run for one-and-a-half hours. T.L.C. showed that the product formation in the two tubes was very similar.

N-(1,2,3,4-Tetrahydroisoquinolin-2-ylmethyl)thiophthalimide with medium-pressure mercury arc

N-(1,2,3,4-Tetrahydroisoquinolin-2-ylmethyl)-thiophthalimide (2.00g, 0.0065 moles) was dissolved in acetonitrile (440 cm³) and irradiated according to method (ii) for one-and-a-quarter hours. The reaction was followed by T.L.C., using 5% methanol/chloroform as eluant. A very small quantity of β -isoindigo was seen to precipitate out, but this was too small to be isolated. The solvent was removed from the reaction mixture in vacuo, and the mixture was separated by column chromatography using analar chloroform as the initial eluant, gradually increasing the polarity to 4% analar methanol/chloroform. Eight fractions were obtained. The first fraction showed an absorption in the ¹H-NMR at δ 9.45, indicating a thioformamide product, crude yield 18 mg (1-2%).

The third was separated on a further column, with analar chloroform as the eluant. One fraction was obtained which contained largely one component. Recrystallisation from absolute ethanol did not lead to a pure sample, and so characterisation was carried out on the impure sample (details below). Despite extensive attempts at separation and purification, no pure products could be obtained from this reaction.

This reaction was repeated, but again no pure products could be isolated and characterised.

Product

m.t. colour change from white to red at 203 °C, melts 212 - 214 °C. IR (1.5% KBr disc) $\bar{\nu}/\text{cm}^{-1}$: 3220, 3090, 2950, 1715, 1615, 1470, 1350, 1325, 1270, 1145, 1105, 1095, 930, 735, 700. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ/ppm : 7.80 - 7.60 (m, 6H), 7.10 (d, $J = 5 \text{ Hz}$, 2H), 6.75 (m, 1H), 6.10 (broad s, 1H), 5.75 (d, $J = 8 \text{ Hz}$, 1H), 4.80 (d, $J = 10 \text{ Hz}$, $1\frac{1}{2}\text{H}$), 4.55 (d, $J = 10 \text{ Hz}$ and s, 2H), 3.15 (m, 5H), 1.65 (broad s, $1\frac{1}{2}\text{H}$). $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ/ppm : 134.3, 133.0, 129.0, 127.9, 126.0, 124.8, 123.7, 123.6, 122.8, 61.8, 46.1, 29.7, 29.2. M.S.: shows that two components are present, of which one looks like phthalimide:²⁴³ m/z 147 (M^+ , base peak), 104, 103 ($\text{M}^+ - \text{CO}_2$), 76. The other is m/z 145 (base, 145.089; $\text{C}_{10}\text{H}_{11}\text{N}$ requires 145.089), 117, 103.

N-(1,2,3,4-Tetrahydroisoquinolin-2-ylmethyl)thiophthalimide
with high-pressure mercury arc

N-(1,2,3,4-Tetrahydroisoquinolin-2-ylmethyl)thiophthalimide (0.43g, 0.0014 moles) was dissolved in acetonitrile (440 cm^3) and irradiated according to method (iii); the cut-off of the filter solution was about 470 nm. The reaction was followed by

T.L.C. using 5% methanol/chloroform as the eluant, and was stopped after three-and-a-half hours. Both ^1H -NMR and T.L.C. showed that the products were a multi-component mixture, and so no separation was done.

N-(1,2,3,4-Tetrahydroisoquinolin-2-ylmethyl)thiophthalimide in benzene

N-(1,2,3,4-Tetrahydroisoquinolin-2-ylmethyl)thiophthalimide (0.20g, 6.5×10^{-4} moles) was dissolved in benzene (105 cm^3) and irradiated according to method (i). The reaction was monitored by T.L.C. using 5% methanol/chloroform as eluant, and was run for half-an-hour. T.L.C. showed that a large number of products had been formed, and that the product distribution appeared similar to that for the acetonitrile solution; the product mixture was not separated.

N-(Dibenzylaminomethyl)thiophthalimide in acetonitrile

N-(Dibenzylaminomethyl)thiophthalimide (0.20g, 5.4×10^{-4} moles) was dissolved in acetonitrile (105 cm^3) and irradiated according to method (i). The reaction was followed by T.L.C. using 5% methanol/chloroform as eluant, and was run for one hour. Separation of the multi-component product mixture by column chromatography did not yield any pure product fractions.

N-(Dibenzylaminomethyl)thiophthalimide in benzene

N-(Dibenzylaminomethyl)thiophthalimide (0.20g, 5.4×10^{-4} moles) was dissolved in benzene (105 cm^3) and irradiated according to method (i). The reaction was followed by T.L.C. using 5% methanol/chloroform as eluant, and was run for one hour. Separation of the multi-component product mixture by column chromatography did not yield any pure product fractions.

It was noted that the appearance of the T.L.C. plate showed a similar multicomponent mixture to that which had been formed for the acetonitrile case.

N-(Dicyclohexylaminomethyl)thiophthalimide

N-(Dicyclohexylaminomethyl)thiophthalimide (0.20g, 5.6×10^{-4} moles) was dissolved in acetonitrile (105 cm³) and irradiated according to method (i). The reaction was followed by T.L.C. using 5% methanol/chloroform as eluant, and was run for five-and-a-half hours, by which time the starting material was shown to have reacted completely (T.L.C.). Some precipitation of a bright yellow solid was observed, but the quantity was too small to measure. T.L.C. showed that the soluble products were a multi-component mixture, and they were not separated.

N-(2-Morpholinoethyl)thiophthalimide

N-(2-Morpholinoethyl)thiophthalimide (0.67g, 0.0024 moles) was dissolved in acetonitrile (105 cm³) and irradiated according to method (i). The reaction was monitored by T.L.C. using 5% methanol/chloroform as eluant, and was stopped after seven-and-a-half hours, by which time all of the starting material appeared to have reacted. T.L.C. showed that a multi-component mixture had formed. Despite extensive attempts at purification by column chromatography and recrystallisation, no pure products could be isolated.

N-(2-Morpholinoethyl)dithiophthalimide

N-(2-Morpholinoethyl)dithiophthalimide (0.18g, 6.2×10^{-4} moles) was dissolved in acetonitrile (105 cm³) and irradiated according to method (i). The reaction was monitored by T.L.C.,

using 5% methanol/chloroform as the eluant, and was stopped after four-and-a-half hours when all of the starting material seemed to have disappeared. T.L.C. showed that a multi-component mixture had been formed. The product mixture was separated by column chromatography, but all of the fractions which were obtained proved to be small (< 30 mg) and impure.

Reaction of 2-benzyl-9b-hydroxy-1-phenyl-2,3,5,9b-tetrahydro-1H-imidazo[4,3-a]isoindol-5-one with Lawesson's reagent

2-Benzyl-9b-hydroxy-1-phenyl-2,3,5,9b-tetrahydro-1H-imidazo[4,3-a]isoindol-5-one (1.78g, 0.0050 moles) was refluxed in toluene (50 cm³) with Lawesson's reagent (1.01g, 0.0025 moles) for one hour. After cooling, the solvent was removed in vacuo, and the mixture was separated by column chromatography, using 1:1 chloroform:toluene as the initial eluant and gradually increasing the polarity to 22% methanol/chloroform, to yield eight fractions. ¹H-NMR spectra of the fractions showed that both aromatic and aliphatic protons were present in all, and IR spectra showed the presence of a carbonyl group in each case. None of the fractions were purified further.

CHAPTER EIGHT

PHOTOCHEMISTRY OF THIOPHTHALIMIDES

PHOTOPHYSICS

EXPERIMENTAL

Electronic absorption spectra were measured on UV/VIS absorption spectrophotometers as described in the General Experimental Procedures chapter.

Emission spectra were recorded on a Perkin Elmer MPF-4 Fluorescence Spectrophotometer by kind permission of Dr. A. Harriman, Davy Faraday Research Laboratory, The Royal Institution, London. A rotating light chopper was added to the spectrophotometer for lifetime measurements. The standard used for the quantum yield measurements was zinc tetraphenylporphyrin.²⁴⁹

Quenching experiments were carried out on a nanosecond transient absorption apparatus by kind permission of Prof. C.A.G.O. Varma and Dr. R.J. Visser, Gorlaeus Laboratories, University of Leiden. The XeCl laser source provides an excitation pulse with a wavelength of 308 nm, and the probing beam is provided by a pulsed 450W xenon lamp. The transient optical density of the sample at the probing wavelength is calculated automatically and determination of the transient optical density at time t at a number of discrete wavelengths gives a profile of the transient absorption spectrum at time t . The decay of the transient optical density may also be fitted numerically to a single exponential decay curve. A full description of this apparatus is given elsewhere.^{198,251}

The solvents used for the standard electronic absorption spectra were of GPR grade. For the emission spectra the solvents were absolute alcohol (100%, James Burrough Ltd.) and methylcyclohexane (Spectrosol grade, BDH Ltd.). Dichloromethane (Analar grade, BDH Ltd.) was used for the quenching measurements and transient absorption spectra.

CHAPTER NINE

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